I. Thermodynamics

I.A Fundamental definitions

• **Thermodynamics** *is a phenomenological description of equilibrium properties of macroscopic systems.*

⋆ As a *phenomenological* description, it is based on a number of empirical observations which are summarized by the laws of thermodynamics. A coherent logical and mathematical structure is then constructed on the basis of these observations, which leads to a variety of useful concepts, and to testable relationships among various quantities. The laws of thermodynamics can only be justified by a more fundamental (microscopic) theory of nature. For example, statistical mechanics attempts to obtain these laws starting from classical or quantum mechanical equations for the evolution of collections of particles.

⋆ A system under study is said to be in *equilibrium* when its properties do not change appreciably with time over the intervals of interest (observation times). The dependence on the observation time makes the concept of equilibrium subjective. For example, window glass is in equilibrium as a solid over many decades, but flows like a fluid over time scales of millennia. At the other extreme, it is perfectly legitimate to consider the equilibrium between matter and radiation in the early universe during the first minutes of the big bang.

⋆ The *macroscopic system* in equilibrium is characterized by a number of *thermodynamic coordinates* or *state functions*. Some common examples of such coordinates are pressure and volume (for a fluid), surface tension and area (for a film), tension and length (for a wire), electric field and polarization (for a dielectric), $\cdots$. A *closed* system is an idealization similar to a point particle in mechanics in that it is assumed to be completely isolated by *adiabatic walls* that don't allow any exchange of heat with the surroundings. By contrast, *diathermic walls* allow heat exchange for an *open* system. In addition to the above mechanical coordinates, the laws of thermodynamics imply the existence of other equilibrium state functions as described in the following sections.

I.B The zeroth law

The zeroth law of thermodynamics describes the transitive nature of thermal equilibrium. It states:

• *If two systems, A and B, are separately in equilibrium with a third system C, then they are also in equilibrium with one another.*

Despite its apparent simplicity, the zeroth law has the consequence of implying the existence of an important state function, the *empirical temperature* Θ, such that systems in equilibrium are at the same temperature.

Proof: Let the equilibrium state of systems A, B, and C be described by the coordinates $\{A_1, A_2, \cdots\}$, $\{B_1, B_2, \cdots\}$, and $\{C_1, C_2, \cdots\}$ respectively. The assumption that A and C are in equilibrium implies a constraint between the coordinates of A and C, i.e. a change in A_1 must be accompanied by some changes in $\{A_2, \cdots; C_1, C_2, \cdots\}$ to maintain equilibrium of A and C. Denote this constraint by

$$f_{AC}(A_1, A_2, \cdots; C_1, C_2, \cdots) = 0. \tag{I.1}$$

The equilibrium of B and C implies a similar constraint

$$f_{BC}(B_1, B_2, \cdots; C_1, C_2, \cdots) = 0. \tag{I.2}$$

Each of the above equations can be solved for C_1 to yield

$$\begin{aligned} C_1 =& F_{AC}(A_1, A_2, \cdots; C_2, \cdots), \\ C_1 =& F_{BC}(B_1, B_2, \cdots; C_2, \cdots). \end{aligned} \tag{I.3}$$

Thus if C is separately in equilibrium with A and B we must have

$$F_{AC}(A_1, A_2, \cdots; C_2, \cdots) = F_{BC}(B_1, B_2, \cdots; C_2, \cdots). \tag{I.4}$$

However, according to the zeroth law there is also equilibrium between A and B, implying the constraint

$$f_{AB}(A_1, A_2, \cdots; B_1, B_2, \cdots) = 0. \tag{I.5}$$

Therefore it must be possible to simplify eq.(I.4) by cancelling the coordinates of C. Hence, the condition (I.5) for equilibrium of A and B must be expressible as

$$\Theta_A(A_1, A_2, \cdots) = \Theta_B(B_1, B_2, \cdots), \tag{I.6}$$

i.e., equilibrium is characterized by a function Θ of thermodynamic coordinates. This function specifies the *equation of state*, and *isotherms* of A are described by the condition $\Theta_A(A_1, A_2, \cdots) = \Theta$.

Example: Consider three systems: (A) a wire of length L with tension F, (B) a paramagnet of magnetization M in a magnetic field B, and (C) a gas of volume V at pressure P. Observations indicate that when these systems are in equilibrium, the following constraints are satisfied between their coordinates:

$$\begin{aligned} \left(P + \frac{a}{V^2}\right)(V-b)(L-L_0) - c[F - K(L-L_0)] = 0, \\ \left(P + \frac{a}{V^2}\right)(V-b)M - dB = 0. \end{aligned} \tag{I.7}$$

Clearly these constraints can be organized into three empirical temperature functions as

$$\Theta \propto \left(P + \frac{a}{V^2}\right)(V-b) = c\left(\frac{F}{L-L_0} - K\right) = d\frac{B}{M}. \tag{I.8}$$

These are the well known equations of state describing:

$$\begin{cases} \left(P + a/V^2\right)(V-b) = Nk_BT & \text{(van der Waals gas)} \\ M = (N\mu_B^2 B)/(3k_BT) & \text{(Curie paramagnet)} \\ F = (K + DT)(L - L_0) & \text{(Hook's law for rubber)} \end{cases} . \tag{I.9}$$

The ideal gas temperature scale: As the above example indicates, the zeroth law merely states the presence of isotherms. In order to set up a practical temperature scale at this stage, a reference system is necessary. The *ideal gas* occupies an important place in thermodynamics and provides the necessary reference. Empirical observations indicate that the product of pressure and volume is constant along the isotherms of any gas that is sufficiently dilute. The ideal gas refers to this *dilute* limit of real gases, and the ideal gas temperature is proportional to the product. The constant of proportionality is determined by reference to the temperature of the triple point of the ice–water–gas system, which was set to 273.16 degrees Kelvin (^0K) by the 10^{th} General Conference on Weights and Measures in 1954. Using a dilute gas (i.e. as $P \to 0$) as thermometer, the temperature of a system can be obtained from

$$T(^oK) \equiv 273.16 \times \left(\lim_{P\to 0} (PV)_{\text{system}} / \lim_{P\to 0} (PV)_{\text{ice-water-gas}} \right). \tag{I.10}$$

I.C The First law

We now consider transformations between different equilibrium states. Such transformations can be achieved by applying *work* or *heat* to the system. The first law states that both work and heat are forms of *energy*, and that the total energy is conserved. We shall use the following formulation:

• *The amount of work required to change the state of an otherwise adiabatically isolated system depends only on the initial and final states, and not on the means by which the work is performed, or on the intermediate stages through which the system passes.*

As a consequence, we conclude the existence of another state function, the internal energy, $E(\mathbf{X})$. Up to a constant, $E(\mathbf{X})$ can be obtained from the amount of work ΔW needed for an *adiabatic* transformation from an initial state $\mathbf{X_i}$ to a final state $\mathbf{X_f}$, using

$$\Delta W = E(\mathbf{X_f}) - E(\mathbf{X_i}). \tag{I.11}$$

In a generic (*non–adiabatic*) transformation, the amount of work does not equal to the change in the internal energy. The difference $\Delta Q = \Delta E - \Delta W$ is defined as the heat intake of the system from its surroundings. Clearly in such transformations, ΔQ and ΔW are not separately functions of state, in that they depend on external factors such as the means of applying work, and not only on the final states. To emphasize this, for a differential transformation we write

$$đQ = dE - đW, \tag{I.12}$$

where $dE = \sum_i \partial_i E dX_i$ can be obtained by differentiation, while $đQ$ and $đW$ generally can not. Also note the convention that the signs of work and heat are chosen to indicate the energy *added* to the system, and not vice versa.

A *quasi-static* transformation is one that is performed sufficiently slowly so that the system is always in equilibrium. Thus at any stage of the process, the thermodynamic coordinates of the system exist and can in principle be computed. For such transformations, the work done on the system (equal in magnitude but opposite in sign to the work done by the system) can be related to changes in these coordinates. Typically one can divide the state functions $\{\mathbf{X}\}$ into a set of *generalized displacements* $\{\mathbf{x}\}$, and their conjugate *generalized forces* $\{\mathbf{J}\}$, such that for an infinitesimal quasi-static transformation

$$đW = \sum_i J_i dx_i. \tag{I.13}$$

Table [1] provides some common examples of such coordinates. Note that the displacement is usually an *extensive* quantity, i.e. proportional to system size, while the forces are *intensive* and independent of size. Also note that pressure is by convention calculated from the force exerted by the system on the walls, as opposed to the force on a spring which is exerted in the opposite direction. This is the origin of the negative sign that usually accompanies hydrostatic work.

System	Force		Displacement	
Wire	Tension	F	Length	L
Film	Surface Tension	$\mathcal{S}$	Area	A
Fluid	Pressure	$-P$	Volume	V
Magnet	Magnetic Field	H	Magnetization	M
Dielectric	Electric Field	E	Polarization	P
Chemical Reaction	Chemical Potential	μ	Particle Number	N

Table 1: Generalized Forces and Displacements

Joule's Free Expansion Experiment: Another important property of the ideal gas is the behavior of its internal energy. Observations indicate that if such a gas expands adiabatically (but not necessarily quasi-statically), from a volume V_i to V_f, the initial and final temperatures are the same. Since the transformation is adiabatic ($\Delta Q = 0$) and there is no external work done on the system ($\Delta W = 0$), the internal energy of the gas is unchanged. Since the pressure and volume of the gas change in the process, but its temperature does not, we conclude that the internal energy depends only on temperature, i.e. $E(V,T) = E(T)$. This property of the ideal gas is in fact a consequence of the form of its equation of state as will be proved in test 1 review problems.

Response functions are the usual method for characterizing the macroscopic behavior of a system. They are experimentally measured from the changes of thermodynamic coordinates with external probes. Some common response functions are:
Heat Capacities are obtained from the change in temperature upon addition of heat to the system. Since heat is not a function of state, the path by which it is supplied must also be specified. For example, for a gas we can calculate the heat capacities at constant volume or pressure, denoted by $C_V = đQ/dT|_V$ and $C_P = đQ/dT|_P$ respectively. The latter is larger since some of the heat is used up in the work done in changes of volume:

$$\begin{aligned} C_V &= \left.\frac{đQ}{dT}\right|_V = \left.\frac{dE - đW}{dT}\right|_V = \left.\frac{dE + PdV}{dT}\right|_V = \left.\frac{\partial E}{\partial T}\right|_V , \\ C_P &= \left.\frac{đQ}{dT}\right|_P = \left.\frac{dE - đW}{dT}\right|_P = \left.\frac{dE + PdV}{dT}\right|_P = \left.\frac{\partial E}{\partial T}\right|_P + P \left.\frac{\partial V}{\partial T}\right|_P . \end{aligned} \tag{I.14}$$

Force Constants measure the (infinitesimal) ratio of displacement to force and are generalizations of the spring constant. Examples include the isothermal compressibility of a gas $\kappa_T = -\partial V/\partial P|_T /V$, and the susceptibility of a magnet $\chi_T = \partial M/\partial B|_T /V$. From the equation of state of an ideal gas $PV \propto T$, we obtain $\kappa_T = 1/P$.
Thermal Responses probe the change in the thermodynamic coordinates with temperature. For example, the expansivity of a gas is given by $\alpha_P = \partial V/\partial T|_P /V$, which equals $1/T$ for the ideal gas.

Since the internal energy of an ideal gas depends only on its temperature, $\partial E/\partial T|_V = \partial E/\partial T|_P = dE/dT$, and eq.(I.14) simplifies to

$$C_P - C_V = P \left.\frac{\partial V}{\partial T}\right|_P = PV\alpha_P = \frac{PV}{T} \equiv Nk_B. \tag{I.15}$$

The last equality follows from extensivity: for a given amount of ideal gas, the constant PV/T is proportional to N, the number of particles in the gas; the ratio is Boltzmann's constant with a value of $k_B \approx 1.4 \times 10^{-23} J^0 K^{-1}$.

I.D The Second Law

The historical development of thermodynamics follows the industrial revolution in the 19^{th} century, and the advent of heat engines. It is interesting to see how such practical considerations as the efficiency of engines can lead to abstract ideas like entropy.

An idealized *heat engine* works by taking in a certain amount of heat Q_H, from a heat source (for example a coal fire), converting a portion of it to work W, and dumping the remaining heat Q_C into a heat sink (e.g. atmosphere). The efficiency of the engine is calculated from

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \leq 1. \tag{I.16}$$

An idealized *refrigerator* is like an engine running backward, i.e. using work W to extract heat Q_C from a cold system, and dumping heat Q_H at a higher temperature. We can similarly define a figure of merit for the performance of a refrigerator as

$$\omega = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}. \tag{I.17}$$

The first law rules out so called 'perpetual motion machines of the first kind', i.e. engines that produce work without consuming any energy. However, the conservation of energy is not violated by an engine that produces work by converting water to ice. Such a 'perpetual motion machine of the second kind' would certainly solve the world's energy problems, but is ruled out by the second law of thermodynamics. The observation that the natural direction for the flow of heat is from hotter to colder bodies is the content of the second law of thermodynamics. There are a number of different formulations of the second law, such as the following two statements.

• **Kelvin's Statement:** *No process is possible whose sole result is the complete conversion of heat into work.*

• **Clausius's Statement:** *No process is possible whose sole result is the transfer of heat from a colder to a hotter body.*

A perfect engine is ruled out by the first statement, a perfect refrigerator by the second. In fact the two statements are equivalent as shown below.

Proof of the equivalence of the Kelvin and Clausius statements proceeds by showing that if one is violated so is the other.

(a) Let us assume that there is a machine that violates Clausius's statement by taking heat Q from a cooler temperature T_C to a higher temperature T_H. Now consider an engine operating between these two temperature, taking heat Q_H from T_H and

dumping Q_C at T_C. The combined system takes $Q_H - Q$ from T_H, produces work equal to $Q_H - Q_C$ and dumps $Q_C - Q$ at T_C. If we adjust the engine output such that $Q_C = Q$, the net result is a 100% efficient engine, in violation of Kelvin's statement. (b) Alternatively, assume a machine that violates Kelvin's law by taking heat Q and converting it completely to work. The work output of this machine can be used to run a refrigerator, with the net outcome of transferring heat from a colder to a hotter body, in violation of Clausius's statement.

Although these statements may appear as rather trivial and qualitative descriptions, they have important quantitative implications as demonstrated in the next sections.

I.E Carnot Engines & Thermodynamic Temperature

• *A Carnot Engine is any engine that is reversible, runs in a cycle, with all of its heat exchanges taking place at a source temperature T_H, and a sink temperature T_C.*

A *reversible* process is one that can be run backward in time by simply reversing its inputs and outputs. It is the thermodynamic equivalent of frictionless motion in mechanics. Since time reversibility implies equilibrium, a reversible transformation must be quasi-static, but the reverse is not necessarily true (e.g., if there is energy dissipation due to friction). An engine that runs in a *cycle* returns to its original internal state at the end of the process. The distinguishing characteristic of the Carnot engine is that heat exchanges with the surroundings are carried out only at two temperatures. The zeroth law allows us to select two isotherms at temperatures T_H and T_C for these heat exchanges. To complete the Carnot cycle we have to connect these isotherms by reversible *adiabatic* paths in the coordinate space. Since heat is not a function of state, we don't know how to construct such paths in general. Fortunately, we have sufficient information at this point to construct a Carnot engine using an ideal gas as its internal working substance. For the purpose of demonstration, let us compute the adiabatic curves for a monatomic ideal gas with an internal energy

$$E = \frac{3}{2} N k_B T = \frac{3}{2} PV.$$

Along a quasi-static path

$$đQ = dE - đW = d(\frac{3}{2}PV) + PdV = \frac{5}{2}PdV + \frac{3}{2}VdP. \tag{I.18}$$

The adiabatic condition $đQ = 0$, then implies a path

$$\frac{dP}{P} + \frac{5}{3}\frac{dV}{V} = 0, \quad \Longrightarrow \quad PV^\gamma = \text{constant}, \tag{I.19}$$

with $\gamma = 5/3$. The adiabatic curves are clearly distinct from the isotherms, and we can select two such curves to intersect our isotherms, thereby completing a Carnot cycle. The assumption of $E \propto T$ is not necessary, and in the test 1 review problems you will construct adiabatics for any $E(T)$. In fact, a similar construction is possible for any two parameter system with $E(J, x)$.

• **Carnot's Theorem:** *No engine operating between two reservoirs (at temperatures T_H and T_C) is more efficient than a Carnot engine operating between them.*

Proof: Since a Carnot engine is reversible, it can be run backward as a refrigerator. Use the non-Carnot engine to run the Carnot engine backward. Let us denote the heat exchanges of the non-Carnot and Carnot engines by Q_H, Q_C, and Q'_H, Q'_C, respectively. The net effect of the two engines is to transfer heat equal to $Q_H - Q'_H = Q_C - Q'_C$ from T_H to T_C. According to Clausius's statement, the quantity of transferred heat cannot be negative, i.e. $Q_H \geq Q'_H$. Since the same quantity of work W, is involved in this process, we conclude that

$$\frac{W}{Q_H} \leq \frac{W}{Q'_H}\,, \quad \Longrightarrow \quad \eta_{\rm Carnot} \geq \eta_{\rm non-Carnot}. \tag{I.20}$$

Corollary: All reversible (Carnot) engines have the same *universal* efficiency $\eta(T_H, T_C)$, since each can be used to run the other one backward.

The Thermodynamic Temperature Scale: As shown earlier, it is at least theoretically possible to construct a Carnot engine using an ideal gas (or any other two parameter system) as working substance. We now find that independent of the material used, and design and construction, all such cyclic and reversible engines have the same maximum theoretical efficiency. Since this maximum efficiency is only dependent on the two temperatures, it can be used to construct a temperature scale. Such a temperature scale has the attractive property of being independent of the properties of any material (e.g. the ideal gas). To construct such a scale we first find out how $\eta(T_H, T_C)$ depends on the two temperatures. Consider two Carnot engines running in series, one between temperatures T_1 and T_2, and the other between T_2 and T_3 ($T_1 > T_2 > T_3$). Denote the heat exchanges, and work outputs, of the two engines by Q_1, Q_2, W_{12}, and Q_2, Q_3, W_{23} respectively. Note that the heat dumped by the first engine is taken in by the second, so that the combined effect is another Carnot engine (since each component is reversible) with heat exchanges Q_1, Q_3, and work output $W_{13} = W_{12} + W_{23}$. The three heats are related by

$$Q_2 = Q_1 - W_{12} = Q_1[1 - \eta(T_1, T_2)],$$

$$Q_3 = Q_2 - W_{23} = Q_2[1-\eta(T_2,T_3)] = Q_1[1-\eta(T_1,T_2)][1-\eta(T_2,T_3)],$$

$$Q_3 = Q_1 - W_{13} = Q_2[1-\eta(T_1,T_3)].$$

Comparison of the final two expressions yields

$$[1-\eta(T_1,T_3)] = [1-\eta(T_1,T_2)][1-\eta(T_2,T_3)]. \tag{I.21}$$

This property implies that $1-\eta(T_1,T_2)$ can be written as a ratio of the form $f(T_2)/f(T_1)$, which by convention is set to T_2/T_1, i.e.

$$\begin{aligned} 1-\eta(T_1,T_2) &= \frac{Q_2}{Q_1} \equiv \frac{T_2}{T_1}, \\ \Longrightarrow \eta(T_H,T_C) &= \frac{T_H - T_C}{T_H}. \end{aligned} \tag{I.22}$$

Eq.(I.22) defines temperature up to a constant of proportionality, which is again set by choosing the triple point of water, ice, and steam to $273.16^0 K$. Throughout this chapter, I have used the symbols Θ and T interchangeably. In fact, by running a Carnot cycle for a perfect gas, it can be proved (see test 1 review problems) that the ideal gas and thermodynamic temperature scales are equivalent. Clearly the thermodynamic scale is not useful from a practical stand-point; its advantage is conceptual, in that it is independent of the properties of any substance. All thermodynamic temperatures are positive, since according to eq.(I.22) the heat extracted from a temperature T is proportional to it. If a negative temperature existed, an engine operating between it and a positive temperature would extract heat from both reservoirs and convert the sum total to work, in violation of Kelvin's statement of the second law.

I.F Entropy

The following theorem allows us to construct another function of state using the second law.

• **Clausius's Theorem:** *For any cyclic transformation (reversible or not),* $\oint đQ/T \leq 0$, *where* $đQ$ *refers to the heat increment supplied to the system at temperature* T.

Proof: We can subdivide the cycle into a series of infinitesimal transformations in which the system receives energy in the form of heat $đQ$ and work $đW$. The system need not be in equilibrium at each interval. Direct all the heat exchanges of the system to one port of a Carnot engine, which has another reservoir at a fixed temperature T_0. Since the sign

of $đQ$ is not specified, the Carnot engine must operate a series of infinitesimal cycles in either direction. To deliver heat $đQ$ to the system at some stage, the engine has to extract heat $đQ_R$ from the fixed reservoir. If the heat is delivered to a part of the system which is locally at a temperature T, then according to eq.(I.22),

$$đQ_R = T_0 \frac{đQ}{T}. \tag{I.23}$$

After the cycle in completed, the system and the Carnot Engine return to their original states. The net effect of the combined process is extracting heat $Q_R = \oint đQ_R$ from the reservoir and converting it to external work W. The work $W = Q_R$ is the sum total of the work elements done by the Carnot engine, *and* the work performed by the system in the complete cycle. By Kelvin's statement of the second law, $Q_R = W \leq 0$, i.e.

$$T_0 \oint \frac{đQ}{T} \leq 0, \quad \Longrightarrow \quad \oint \frac{đQ}{T} \leq 0, \tag{I.24}$$

since $T_0 > 0$. Note that T in eq.(I.24) refers to the temperature of the whole system only for quasi-static processes in which it can be uniquely defined throughout the cycle. Otherwise, it is just a local temperature (say at a boundary of the system) at which the Carnot engine deposits the element of heat.

Consequences of Clausius's theorem:

(1) For a *reversible cycle* $\oint đQ_{\rm rev}/T = 0$, since by running the cycle in the opposite direction $đQ_{\rm rev} \to -đQ_{\rm rev}$, and by the above theorem $đQ_{\rm rev}/T$ is both non-negative and non-positive, hence zero. This result implies that the integral of $đQ_{\rm rev}/T$ between any two points A and B is independent of path, since for two paths (1) and (2)

$$\int_A^B \frac{đQ^{(1)}_{\rm rev}}{T_1} + \int_B^A \frac{đQ^{(2)}_{\rm rev}}{T_2} = 0, \quad \Longrightarrow \int_A^B \frac{đQ^{(1)}_{\rm rev}}{T_1} = \int_A^B \frac{đQ^{(2)}_{\rm rev}}{T_2}. \tag{I.25}$$

(2) Using eq.(I.25) we can construct yet another function of state, the *entropy* S. Since the integral is independent of path, and only depends on the two end points, we can set

$$S(B) - S(A) \equiv \int_A^B \frac{đQ_{\rm rev}}{T}. \tag{I.26}$$

For reversible processes, we can now compute the heat from $đQ_{\rm rev} = TdS$. This allows us to construct adiabatic curves for a general (multi-variable) system from the condition of constant S. Note that eq.(I.26) only defines the entropy up to an overall constant.

(3) Consider an irreversible change from A to B. Make a complete cycle by returning from B to A along a reversible path. Then

$$\int_A^B \frac{đQ}{T} + \int_B^A \frac{đQ_{\rm rev}}{T} \leq 0\,, \quad \Longrightarrow \quad \int_A^B \frac{đQ}{T} \leq S(B) - S(A). \tag{I.27}$$

In differential form, this implies that $dS \geq đQ/T$ for any transformation. In particular, consider adiabatically isolating a number of subsystems, each initially separately in equilibrium. As they come to a state of joint equilibrium, since the net $đQ = 0$, we must have $\delta S \geq 0$. Thus an adiabatic system attains a maximum value of entropy in equilibrium since spontaneous internal changes can only increase S. The direction of increasing entropy thus points out the arrow of time, and the path to equilibrium.

(4) For a reversible (hence quasi-static) transformation, $đQ = TdS$ and $đW = \sum_i J_i dx_i$, and the first law implies

$$dE = đQ + đW = TdS + \sum_i J_i dx_i\,. \tag{I.28}$$

Although eq.(I.28) was obtained from a reversible transformation, as a relation between functions of state it is a generally valid identity of thermodynamics. Also note that in this equation S and T appear as conjugate variables, with S playing the role of a displacement, and T as the corresponding force.

(5) The number of *independent variables* necessary to describe a thermodynamic system also follows from eq.(I.28). If there are n methods of doing work on a system, represented by n conjugate pairs (J_i, x_i), then $n+1$ independent coordinates are necessary to describe the system. (We shall ignore possible constraints between the mechanical coordinates.) For example, choosing $(E, \{x_i\})$ as coordinates, it follows from eq.(I.28) that

$$\left.\frac{\partial S}{\partial E}\right|_{\mathbf{x}} = \frac{1}{T}, \quad \text{and} \quad \left.\frac{\partial S}{\partial x_i}\right|_{E, x_{j\neq i}} = -\frac{J_i}{T}. \tag{I.29}$$

($\mathbf{x}$ and $\mathbf{J}$ will be used as short–hand notations for the parameter sets $\{x_i\}$ and $\{J_i\}$.)

I.G Approach to Equilibrium and Thermodynamic Potentials

Evolution of non-equilibrium systems towards equilibrium is governed by the second law of thermodynamics. For example, in the previous section we showed that for an adiabatically isolated system entropy must increase in any spontaneous change and reaches a maximum in equilibrium. What about out of equilibrium systems that are not adiabatically isolated and which may also be subject to external mechanical work? It is usually possible to define other thermodynamic potentials that are extremized when the system is in equilibrium.

Enthalpy is the appropriate function when there is no heat exchange ($đQ = 0$), and the system comes to mechanical equilibrium with a *constant external force*. The minimum enthalpy principle merely formulates the observation that stable mechanical equilibrium is obtained by minimizing the net potential energy of the system plus the external agent. For example, consider a spring of natural extension L_0 and spring constant K, subject to the force exerted by a particle of mass m. For an extension $x = L - L_0$, the internal energy of the spring is $Kx^2/2$, while there is a change of $-mgx$ in the potential energy of the particle. Mechanical equilibrium is obtained by minimizing $Kx^2/2 - mgx$ at an extension $x_{\rm eq} = mg/K$. The spring at any other value of the displacement initially oscillates before coming to rest at $x_{\rm eq}$ due to friction. For general displacements $\mathbf{x}$, at constant generalized forces $\mathbf{J}$, the work input to the system is $đW \leq \mathbf{J} \cdot \delta\mathbf{x}$. (Equality is achieved for a reversible change, but there is generally some loss of the external work into friction.) Since $đQ = 0$, using the first law, $\delta E \leq \mathbf{J} \cdot \delta\mathbf{x}$, and

$$\delta H \leq 0, \quad \text{where} \quad H = E - \mathbf{J} \cdot \mathbf{x} \tag{I.30}$$

is the enthalpy. The variations of H *in equilibrium* are given by

$$dH = dE - d(\mathbf{J} \cdot \mathbf{x}) = TdS + \mathbf{J} \cdot d\mathbf{x} - \mathbf{x} \cdot d\mathbf{J} - \mathbf{J} \cdot d\mathbf{x} = TdS - \mathbf{x} \cdot d\mathbf{J} \quad . \tag{I.31}$$

The equality in eq.(I.31), and the inequality in eq.(I.30), are a possible source of confusion. Note that eq.(I.30) refers to variations of H on approaching equilibrium as some parameter that is not a function of state is varied (e.g. the velocity of the particle joined to the spring in the above example). By contrast eq.(I.31) describes a relation between equilibrium coordinates. To differentiate the two cases, I will denoted the former non-equilibrium variations by δ.

The coordinate set $(S, \mathbf{J})$ is the natural choice for describing the enthalpy, and it follows from eq.(I.31) that

$$x_i = -\left.\frac{\partial H}{\partial J_i}\right|_{S, J_{j\neq i}}. \tag{I.32}$$

Variations of the enthalpy with temperature are related to heat capacities at constant force, for example

$$C_P = \left.\frac{đQ}{dT}\right|_P = \left.\frac{dE + PdV}{dT}\right|_P = \left.\frac{d(E+PV)}{dT}\right|_P = \left.\frac{dH}{dT}\right|_P. \tag{I.33}$$

Note, however, that a change of variables is necessary to express H in terms of T, rather than the more natural variable S.

Helmholtz Free energy is useful for isothermal transformations in the absence of mechanical work ($đW = 0$). From Clausius's theorem, the heat intake of a system at a constant temperature T satisfies $đQ \leq T\delta S$. Hence $\delta E = đQ + đW \leq T\delta S$, and

$$\delta F \leq 0, \quad \text{where} \quad F = E - TS \tag{I.34}$$

is the Helmholtz free energy. Since

$$dF = dE - d(TS) = TdS + \mathbf{J}\cdot d\mathbf{x} - SdT - TdS = -SdT + \mathbf{J}\cdot d\mathbf{x}, \tag{I.35}$$

the coordinate set $(T, \mathbf{x})$ (the quantities kept constant during an isothermal transformation with no work) is most suitable for describing the free energy. The equilibrium forces and entropy can be obtained from

$$J_i = \left.\frac{\partial F}{\partial x_i}\right|_{T, x_{j\neq i}}, \quad S = -\left.\frac{\partial F}{\partial T}\right|_{\mathbf{x}}. \tag{I.36}$$

The internal energy can also be calculated from F using

$$E = F + TS = F - T\left.\frac{\partial F}{\partial T}\right|_{\mathbf{x}} = -T^2\left.\frac{\partial (F/T)}{\partial T}\right|_{\mathbf{x}}. \tag{I.37}$$

Gibbs Free Energy applies to isothermal transformations involving mechanical work at constant external force. The natural inequalities for work and heat input into the system are given by $đW \leq \mathbf{J}\cdot\delta\mathbf{x}$ and $đQ \leq T\delta S$. Hence $\delta E \leq T\delta S + \mathbf{J}\cdot\delta\mathbf{x}$ leading to

$$\delta G \leq 0, \quad \text{where} \quad G = E - TS - \mathbf{J}\cdot\mathbf{x} \tag{I.38}$$

is the Gibbs free energy. Variations of G are given by

$$dG = dE - d(TS) - d(\mathbf{J}\cdot\mathbf{x}) = TdS + \mathbf{J}\cdot d\mathbf{x} - SdT - TdS - \mathbf{x}\cdot d\mathbf{J} - \mathbf{J}\cdot d\mathbf{x} = -SdT - \mathbf{x}\cdot d\mathbf{J}, \quad \text{(I.39)}$$

and most easily expressed in terms of $(T, \mathbf{J})$.

	$đQ = 0$	Constant T
$đW = 0$	$\delta S \geq 0$	$\delta F \leq 0$
Constant $\mathbf{J}$	$\delta H \leq 0$	$\delta G \leq 0$

Table 2: Inequalities satisfied by thermodynamic potentials.

Table (2) summarizes the above results on thermodynamic functions. Eqs.(I.30), (I.34), and (I.38) are examples of Legendre transformations, used to change variables to the most natural set of coordinates for describing a particular situation. So far, we implicitly assumed a constant number of particles in the system. In chemical reactions, and in equilibrium between two phases, the number of particles in a given constituent may change. The change in the number of particles necessarily involves changes in the internal energy, which is expressed in terms of a *chemical work* $đW = \mu \cdot d\mathbf{N}$. Here $\mathbf{N} = \{N_1, N_2, \cdots\}$ lists the number of particles of each species, and $\mu = \{\mu_1, \mu_2, \cdots\}$ the associated *chemical potentials* which measure the work necessary to add additional particles to the system. Traditionally, chemical work is treated differently from mechanical work and is not subtracted from E in the Gibbs free energy of eq.(I.38). For chemical equilibrium in circumstances that involve no mechanical work, the appropriate state function is the **Grand Potential** given by

$$\mathcal{G} = E - TS - \mu \cdot \mathbf{N} \quad . \quad \text{(I.40)}$$

$\mathcal{G}(T, \mu, \mathbf{x})$ is minimized in chemical equilibrium, and its variations in general satisfy

$$d\mathcal{G} = -SdT - \mathbf{J}\cdot d\mathbf{x} - \mathbf{N}\cdot d\mu \quad . \quad \text{(I.41)}$$

Example: To illustrate the concepts of this section, consider N particles of supersaturated steam in a container of volume V at a temperature T. How can we describe the approach of steam to an equilibrium mixture with N_w particles in the liquid and N_s particles in the gas phase? The fixed coordinates describing this system are V, T, and N. The appropriate

thermodynamic function from Table (2) is the Helmholtz free energy $F(V,T,N)$, whose variations satisfy

$$dF = d(E - TS) = -SdT - PdV + \mu dN. \tag{I.42}$$

Before the system reaches equilibrium at a particular value of N_w, it goes through a series of non-equilibrium states with smaller amounts of water. If the process is sufficiently slow, we can construct an out of equilibrium value for F as

$$F(V,T,N|N_w) = F_w(T,N_w) + F_s(V,T,N-N_w), \tag{I.43}$$

which depends on an additional variable N_w. (It is assumed that the volume occupied by water is small and irrelevant.) According to eq.(I.34), the equilibrium point is obtained by minimizing F with respect to this variable. Since

$$\delta F = \left.\frac{\partial F_w}{\partial N_w}\right|_{T,V} \delta N_w - \left.\frac{\partial F_s}{\partial N_s}\right|_{T,V} \delta N_w, \tag{I.44}$$

and $\partial F/\partial N|_{T,V} = \mu$ from eq.(I.42), the equilibrium condition can be obtained by equating the chemical potentials, i.e. from $\mu_w(V,T) = \mu_s(V,T)$. The identity of chemical potentials is the condition for chemical equilibrium. Naturally, to proceed further we need expressions for μ_w and μ_s.

I.H Useful Mathematical Results

(1) Extensivity: Including chemical work, variations of the *extensive* coordinates of the system are related by (generalizing eq.(I.28))

$$dE = TdS + \mathbf{J}\cdot d\mathbf{x} + \mu \cdot d\mathbf{N}. \tag{I.45}$$

For fixed intensive coordinates, the extensive quantities are simply proportional to size or to the number of particles. This proportionality is expressed mathematically by

$$E(\lambda S, \lambda \mathbf{x}, \lambda \mathbf{N}) = \lambda E(S,\mathbf{x},\mathbf{N}). \tag{I.46}$$

Evaluating the derivative of the above equation with respect to λ at $\lambda = 1$, results in

$$\left.\frac{\partial E}{\partial S}\right|_{\mathbf{x},\mathbf{N}} S + \sum_i \left.\frac{\partial E}{\partial x_i}\right|_{S,x_{j\neq i},\mathbf{N}} x_i + \sum_\alpha \left.\frac{\partial E}{\partial N_\alpha}\right|_{S,\mathbf{x},N_{\beta\neq\alpha}} N_\alpha = E(S,\mathbf{x},\mathbf{N})\,. \tag{I.47}$$

The partial derivatives in the above equation can be identified from eq.(I.45) as T, J_i, and μ_α respectively. Substituting these values into eq.(I.47) leads to the so called fundamental equation of thermodynamics

$$E = TS + \mathbf{J}\cdot\mathbf{x} + \mu\cdot\mathbf{N}\,. \tag{I.48}$$

Combining the variations of eq.(I.48) with eq.(I.45) leads to a constraint between the variations of intensive coordinates

$$SdT + \mathbf{x}\cdot d\mathbf{J} + \mathbf{N}\cdot d\mu = 0\,, \tag{I.49}$$

known as the *Gibbs–Duhem* relation.

Example: For a fixed amount of gas ($dN = 0$), variations of the chemical potential along an isotherm can be calculated as follows. Since $dT = 0$, the Gibbs-Duhem relation gives $-VdP + Nd\mu = 0$, and

$$d\mu = \frac{V}{N}dP = k_BT\frac{dP}{P}, \tag{I.50}$$

where we have used the ideal gas equation of state $PV = Nk_BT$. Integrating the above equation gives

$$\mu = \mu_0 + k_BT\ln\frac{P}{P_0} = \mu_0 - k_BT\ln\frac{V}{V_0}, \tag{I.51}$$

where (P_0, V_0, μ_0) refer to the coordinates of a reference point.

(2) Maxwell's Relations: Combining the mathematical rules of differentiation with thermodynamic relationships leads to several useful results. The most important of these are Maxwell's relations which follow from the commutative property $[\partial_x\partial_y f(x,y) = \partial_y\partial_x f(x,y)]$ of derivatives. For example, it follows from eq.(I.45) that

$$\left.\frac{\partial E}{\partial S}\right|_{\mathbf{x},\mathbf{N}} = T, \quad \text{and} \quad \left.\frac{\partial E}{\partial x_i}\right|_{S,x_{j\neq i},\mathbf{N}} = J_i. \tag{I.52}$$

The joint second derivative of E is then given by

$$\frac{\partial^2 E}{\partial S\partial x_i} = \frac{\partial^2 E}{\partial x_i\partial S} = \left.\frac{\partial T}{\partial x_i}\right|_S = \left.\frac{\partial J_i}{\partial S}\right|_{x_i}. \tag{I.53}$$

Since $(\partial y/\partial x) = (\partial x/\partial y)^{-1}$, the above equation can be inverted to give

$$\left.\frac{\partial S}{\partial J_i}\right|_{x_i} = \left.\frac{\partial x_i}{\partial T}\right|_S. \tag{I.54}$$

Similar identities can be obtained from the variations of other state functions. Supposing that we are interested in finding an identity involving $\partial S/\partial x|_T$. We would like to find a state function whose variations include SdT and Jdx. The correct choice is $dF = d(E-TS) = -SdT+Jdx$. Looking at the second derivative of F yields the Maxwell relation

$$-\left.\frac{\partial S}{\partial x}\right|_T = \left.\frac{\partial J}{\partial T}\right|_x . \tag{I.55}$$

To calculate $\partial S/\partial J|_T$, consider $d(E-TS-Jx) = -SdT-xdJ$, which leads to the identity

$$\left.\frac{\partial S}{\partial J}\right|_T = \left.\frac{\partial x}{\partial T}\right|_J . \tag{I.56}$$

There are a variety of mnemonics which are supposed to help you remember and construct Maxwell's equations, such as Magic Squares, Jacobians, etc. I personally don't find any of these methods worth learning. The most logical approach is to remember the laws of thermodynamics and hence eq.(I.28), and to then manipulate it so as to find the appropriate derivative using the rules of differentiation.

Example: To obtain $\partial\mu/\partial P|_{N,T}$ for an ideal gas, start with $d(E-TS+PV) = -SdT + VdP + \mu dN$. Clearly

$$\left.\frac{\partial \mu}{\partial P}\right|_{N,T} = \left.\frac{\partial V}{\partial N}\right|_{T,P} = \frac{V}{N} = \frac{k_B T}{P}, \tag{I.57}$$

as in eq.(I.50). From eq.(I.28) it also follows that

$$\left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T} = -\frac{\partial E/\partial V|_{S,N}}{\partial E/\partial S|_{V,N}}, \tag{I.58}$$

where we have used eq.(I.45) for the final identity. The above equation can be rearranged into

$$\left.\frac{\partial S}{\partial V}\right|_{E,N} \left.\frac{\partial E}{\partial S}\right|_{V,N} \left.\frac{\partial V}{\partial E}\right|_{S,N} = -1, \tag{I.59}$$

which is an illustration of the *chain rule* of differentiation.

I.I Stability Conditions

The conditions derived in section I.G are similar to the well known requirements for mechanical stability. A particle moving in an external potential U settles to a stable equilibrium at a minimum value of U. In addition to the vanishing of the force $-U'$, this is a consequence of the loss of energy to frictional processes. Stable equilibrium occurs at a *minimum* of the potential energy. For a thermodynamic system, equilibrium occurs at the extremum of the appropriate potential, for example at the maximum value of entropy for an isolated system. The requirement that spontaneous changes should *always* lead to an increased entropy, places important constraints on equilibrium response functions, discussed in this section.

Consider a homogeneous system at equilibrium, characterized by intensive state functions $(T, \mathbf{J}, \mu)$, and extensive variables $(E, \mathbf{x}, \mathbf{N})$. Now imagine that the system is arbitrarily divided into two *equal* parts, and that one part spontaneously transfers some energy to the other part in the form of work or heat. The two subsystems, A and B, initially have the same values for the intensive variables, while their extensive coordinates satisfy $E_A + E_B = E$, $\mathbf{x}_A + \mathbf{x}_B = \mathbf{x}$, and $\mathbf{N}_A + \mathbf{N}_B = \mathbf{N}$. After the exchange of energy between the two subsystems, the coordinates of A change to

$$(E_A + \delta E,\ \mathbf{x}_A + \delta\mathbf{x},\ \mathbf{N}_A + \delta\mathbf{N}),\ \text{and}\ (T_A + \delta T_A,\ \mathbf{J}_A + \delta\mathbf{J}_A,\ \mu_A + \delta\mu_A), \tag{I.60}$$

and those of B to

$$(E_B - \delta E,\ \mathbf{x}_B - \delta\mathbf{x},\ \mathbf{N}_B - \delta\mathbf{N}),\ \text{and}\ (T_B + \delta T_B,\ \mathbf{J}_B + \delta\mathbf{J}_B,\ \mu_B + \delta\mu_B). \tag{I.61}$$

Note that the overall system is maintained at constant E, $\mathbf{x}$, and $\mathbf{N}$. Since the intensive variables are themselves functions of the extensive coordinates, to *first order* in the variations of $(E, \mathbf{x}, \mathbf{N})$, we have

$$\delta T_A = -\delta T_B \equiv \delta T, \quad \delta\mathbf{J}_A = -\delta\mathbf{J}_B \equiv \delta\mathbf{J}, \quad \delta\mu_A = -\delta\mu_B \equiv \delta\mu. \tag{I.62}$$

Using eq.(I.48), the entropy of the system can be written as

$$S = S_A + S_B = \left(\frac{E_A}{T_A} - \frac{\mathbf{J}_A}{T_A}\cdot\mathbf{x}_A - \frac{\mu_A}{T_A}\cdot\mathbf{N}_A\right) + \left(\frac{E_B}{T_B} - \frac{\mathbf{J}_B}{T_B}\cdot\mathbf{x}_B - \frac{\mu_B}{T_B}\cdot\mathbf{N}_B\right). \tag{I.63}$$

Since by assumption we are expanding about the equilibrium point, the first order changes vanish, and to second order

$$\delta S = \delta S_A + \delta S_B = 2\left[\delta\left(\frac{1}{T_A}\right)\delta E_A - \delta\left(\frac{\mathbf{J}_A}{T_A}\right)\cdot\delta\mathbf{x}_A - \delta\left(\frac{\mu_A}{T_A}\right)\cdot\delta\mathbf{N}_A\right]. \tag{I.64}$$

(We have used eq.(I.62) to note that the second order contribution of B is the same as A.) Eq.(I.64) can be rearranged to

$$\begin{aligned}\delta S =& -\frac{2}{T_A}\left[\delta T_A\left(\frac{\delta E_A - \mathbf{J}_A\cdot\delta\mathbf{x}_A - \mu_A\cdot\delta\mathbf{N}_A}{T_A}\right) + \delta\mathbf{J}_A\cdot\delta\mathbf{x}_A + \delta\mu_A\cdot\delta\mathbf{N}_A\right] \\ =& -\frac{2}{T_A}\left[\delta T_A\delta S_A + \delta\mathbf{J}_A\cdot\delta\mathbf{x}_A + \delta\mu_A\cdot\delta\mathbf{N}_A\right].\end{aligned} \tag{I.65}$$

The condition for stable equilibrium is that any change should lead to a decrease in entropy, and hence we must have

$$\delta T\delta S + \delta\mathbf{J}\cdot\delta\mathbf{x} + \delta\mu\cdot\delta\mathbf{N} \geq 0. \tag{I.66}$$

We have now removed the subscript A, as the above condition must apply to the whole system as well as to any part of it.

The above condition was obtained assuming that the overall system was kept at constant E, $\mathbf{x}$, and $\mathbf{N}$. In fact, since all coordinates appear symmetrically in this expression, the same result is obtained for any other set of constraints. For example, variations in δT and $\delta\mathbf{x}$ with $\delta\mathbf{N} = 0$, lead to

$$\begin{cases} \delta S = \left.\dfrac{\partial S}{\partial T}\right|_{\mathbf{x}}\delta T + \left.\dfrac{\partial S}{\partial x_i}\right|_{T}\delta x_i \\ \delta J_i = \left.\dfrac{\partial J_i}{\partial T}\right|_{\mathbf{x}}\delta T + \left.\dfrac{\partial J_i}{\partial x_j}\right|_{T}\delta x_j \end{cases}. \tag{I.67}$$

Substituting these variations into eq.(I.66) leads to

$$\left.\frac{\partial S}{\partial T}\right|_{\mathbf{x}}(\delta T)^2 + \left.\frac{\partial J_i}{\partial x_j}\right|_{T}\delta x_i\delta x_j \geq 0. \tag{I.68}$$

Note that the cross terms proportional to $\delta T\delta x_i$ cancel due to the Maxwell relation in eq.(I.56). Eq.(I.68) is a *quadratic from*, and must be positive for *all choices* of δT and $\delta\mathbf{x}$. The resulting constraints on the coefficients are independent of how the system was initially partitioned into subsystems A and B, and represent the conditions for stable equilibrium.

If only δT is non-zero, eq.(I.66) requires $\partial S/\partial T|_{\mathbf{x}} \geq 0$, implying a positive heat capacity, since

$$C_{\mathbf{x}} = \left.\frac{đQ}{dT}\right|_{\mathbf{x}} = T \left.\frac{\partial S}{\partial T}\right|_{\mathbf{x}} \geq 0. \tag{I.69}$$

If only one of the δx_i in eq.(I.66) is non-zero, the corresponding response function $\partial x_i/\partial J_i|_{T,x_{j\neq i}}$ must be positive. However, a more general requirement exists since all $\delta\mathbf{x}$ values may be chosen non-zero. The general requirement is that the matrix of coefficients $\partial J_i/\partial x_j|_T$ must be *positive definite*. A matrix is positive definite if all of its eigenvalues are positive. It is necessary, but not sufficient, that all the diagonal elements of such a matrix (the inverse response functions) be positive, leading to further constraints between the response functions. Including chemical work for a gas, the appropriate matrix is

$$\begin{bmatrix} -\left.\frac{\partial P}{\partial V}\right|_{T,N} & -\left.\frac{\partial P}{\partial N}\right|_{T,V} \\ \left.\frac{\partial \mu}{\partial V}\right|_{T,N} & \left.\frac{\partial \mu}{\partial N}\right|_{T,V} \end{bmatrix}. \tag{I.70}$$

In addition to the positivity of the response functions $\kappa_{T,N} = -V^{-1}\,\partial V/\partial P|_{T,N}$ and $\partial N/\partial \mu|_{T,V}$, the determinant of the matrix must be positive, requiring

$$\left.\frac{\partial P}{\partial N}\right|_{T,V} \left.\frac{\partial \mu}{\partial V}\right|_{T,N} - \left.\frac{\partial P}{\partial V}\right|_{T,N} \left.\frac{\partial \mu}{\partial N}\right|_{T,V} \geq 0. \tag{I.71}$$

Another interesting consequence of eq.(I.66) relates to the critical point of a gas where $\partial P/\partial V|_{T_c,N} = 0$. Assuming that the critical isotherm can be analytically expanded as

$$\delta P(T = T_c) = \left.\frac{\partial P}{\partial V}\right|_{T_c,N} \delta V + \frac{1}{2} \left.\frac{\partial^2 P}{\partial V^2}\right|_{T_c,N} \delta V^2 + \frac{1}{6} \left.\frac{\partial^3 P}{\partial V^3}\right|_{T_c,N} \delta V^3 + \cdots, \tag{I.72}$$

the stability condition $-\delta P \delta V \geq 0$ implies that $\partial^2 P/\partial V^2|_{T_c,N}$ must be zero, and the third derivative negative, if the first derivative vanishes. This condition is used to obtain the critical point of the gas from mean-field approximations to the isotherms (such as the van der Waals isotherms). In fact, it is usually not justified to make a Taylor expansion around the critical point as in eq.(I.72), although the constraint $-\delta P \delta V \geq 0$ remains applicable.

I.J The Third Law

Differences in entropy between two states can be computed using the second law, from $\Delta S = \int đQ_{\rm rev}/T$. Low temperature experiments indicate that $\Delta S(\mathbf{X}, T)$ vanishes as T goes to zero for any set of coordinates $\mathbf{X}$. This observation is independent of the other laws of thermodynamics, leading to the formulation of a third law by Nernst, which states

• *The entropy of all systems at zero absolute temperature is a universal constant that can be taken to be zero.*

The above statement actually implies that

$$\lim_{T\to 0} S(\mathbf{X}, T) = 0, \tag{I.73}$$

which is a stronger requirement than the vanishing of the differences $\Delta S(\mathbf{X}, T)$. This extended condition has been tested for metastable phases of a substance. Certain materials such as sulphur or phosphine can exist in a number of rather similar crystalline structures (*allotropes*). Of course, at a given temperature only one of these structures is truly stable. Let us imagine that as the high temperature equilibrium phase A, is cooled slowly, it makes a transition at a temperature T^* to phase B, releasing *latent heat* L. Under more rapid cooling conditions the transition is avoided, and phase A persists in metastable equilibrium. The entropies in the two phases can be calculated by measuring the heat capacities $C_A(T)$ and $C_B(T)$. Starting from $T = 0$, the entropy at a temperature slightly above T^* can be computed along the two possible paths as

$$S(T^* + \epsilon) = S_A(0) + \int_0^{T^*} dT' \frac{C_A(T')}{T'} = S_B(0) + \int_0^{T^*} dT' \frac{C_B(T')}{T'} + \frac{L}{T^*}. \tag{I.74}$$

Such measurements have indeed verified that $S_A(0) = S_B(0) \equiv 0$.

Consequences of the third law:

(1) Since $S(T = 0, \mathbf{X}) = 0$ for all coordinates $\mathbf{X}$,

$$\lim_{T\to 0} \left.\frac{\partial S}{\partial \mathbf{X}}\right|_T = 0. \tag{I.75}$$

(2) Heat capacities must vanish as $T \to 0$ since

$$S(T, \mathbf{X}) - S(0, \mathbf{X}) = \int_0^T dT' \frac{C_{\mathbf{X}}(T')}{T'}, \tag{I.76}$$

and the integral diverges as $T \to 0$ unless

$$\lim_{T\to 0} C_{\mathbf{X}}(T) = 0. \tag{I.77}$$

(3) Thermal expansivities also vanish as $T \to 0$ since

$$\alpha_J = \frac{1}{x}\left.\frac{\partial x}{\partial T}\right|_J = \frac{1}{x}\left.\frac{\partial S}{\partial J}\right|_T. \tag{I.78}$$

The second equality follows from the Maxwell relation in eq.(I.56). The vanishing of the latter is guaranteed by eq.(I.75).

(4) It is impossible to cool any system to absolute zero temperature in a finite number of steps. For example, we can cool a gas by an adiabatic reduction in pressure. Since the curves of S versus T for different pressures must join at $T = 0$, successive steps involve progressively smaller changes, in S and in T, on approaching zero temperature. Alternatively, the unattainability of zero temperatures implies that $S(T = 0, P)$ is independent of P. This is a weaker statement of the third law which also implies the equality of zero temperature entropy for different substances.

In the following sections, we shall attempt to justify the laws of thermodynamics from a microscopic point of view. The first law is clearly a reflection of the conservation of energy, which also operates at the microscopic level. The zeroth and second laws suggest an irreversible approach to equilibrium, a concept that has no analog at the particulate level. It is justified as reflecting the collective behavior of large numbers of degrees of freedom. In statistical mechanics the entropy is calculated as $S = k_B \ln g$, where g is the degeneracy of the states (number of configurations with the same energy). The third law of thermodynamics thus requires that $g = 1$ at $T = 0$, i.e. that the ground state of any system is unique. This condition *does not hold* within the framework of classical statistical mechanics, as there are examples of both non-interacting (such as an ideal gas), and interacting (the frustrated spins in a triangular antiferromagnet) systems with degenerate ground states, and a finite zero temperature entropy. However, classical mechanics is inapplicable at very low temperatures and energies where quantum effects become important. The third law is then equivalent to the statement that the ground state of a quantum mechanical system is unique. While this can be proved for a non-interacting system, there is no general proof of its validity with interactions. Unfortunately, the onset of quantum effects (and other possible origins of the breaking of classical degeneracy) are system specific. Hence it is not a priori clear how low the temperature must be, before the predictions

of the third law can be observed. Another deficiency of the law is its inapplicability to glassy phases. Glasses results from the freezing of supercooled liquids into configurations with extremely slow dynamics. While not truly equilibrium phases (and hence subject to all the laws of thermodynamics), they are effectively so due to the slowness of the dynamics. A possible test of the applicability of the third law to glasses, is discussed in test #1 review problems.

II. Probability

II.A General Definitions

The laws of thermodynamics are based on observations of *macroscopic bodies*, and encapsulate their thermal properties. On the other hand, matter is composed of atoms and molecules whose motions are governed by fundamental laws of classical or quantum mechanics. It should be possible, in principle, to derive the behavior of a macroscopic body from the knowledge of its components. This is the problem addressed by kinetic theory in the following lectures. Actually, describing the full dynamics of the enormous number of particles involved is quite a daunting task. As we shall demonstrate, for discussing equilibrium properties of a macroscopic system, full knowledge of the behavior of its constituent particles is not necessary. All that is required is the *likelihood* that the particles are in a particular microscopic state. Statistical mechanics is thus an inherently *probabilities* description of the system. Familiarity with manipulations of probabilities is therefore an important prerequisite to statistical mechanics. Our purpose here is to review some important results in the theory of probability, and to introduce the notations that will be used in the rest of the course.

The entity under investigation is a *random variable* x, which has a set of possible *outcomes* $\mathcal{S} \equiv \{x_1, x_2, \cdots\}$. The outcomes may be *discrete* as in the case of a coin toss, $S_{\rm coin} = \{\text{head, tail}\}$, or a dice throw, $\mathcal{S}_{\rm dice} = \{1, 2, 3, 4, 5, 6\}$, or *continuous* as for the velocity of a particle in a gas, $\mathcal{S}_{\vec{v}} = \{-\infty < v_x, v_y, v_z < \infty\}$, or the energy of an electron in a metal at zero temperature, $\mathcal{S}_\epsilon = \{0 \leq \epsilon \leq \epsilon_F\}$. An *event* is any subset of outcomes $E \subset \mathcal{S}$, and is assigned a *probability* $p(E)$, e.g. $p_{\rm dice}(\{1\}) = 1/6$, or $p_{\rm dice}(\{1, 3\}) = 1/3$. From an axiomatic point of view, the probabilities must satisfy the following conditions:

(i) *Positivity*: $p(E) \geq 0$, i.e. all probabilities must be non-zero.

(ii) *Additivity*: $p(A \text{ or } B) = p(A) + p(B)$, if A and B are disconnected events.

(iii) *Normalization*: $p(\mathcal{S}) = 1$, i.e. the random variable must have some outcome in $\mathcal{S}$.

From a practical point of view, we would like to know how to assign probability values to various outcomes. There are two possible approaches:

(1) *Objective* probabilities are obtained *experimentally* from the relative frequency of the occurrence of an outcome in many tests of the random variable. If the random process is repeated N times, and the event A occurs N_A times, then

$$p(A) = \lim_{N\to\infty} \frac{N_A}{N}.$$

For example, a series of $N = 100,\ 200,\ 300$ throws of a dice may result in $N_1 = 19,\ 30,\ 48$ occurrences of 1. The ratios .19, .15, .16 provide an increasingly more reliable estimate of the probability $p_{\rm dice}(\{1\})$.

(2) *Subjective* probabilities provide a *theoretical* estimate based on the uncertainties related to lack of precise knowledge of outcomes. For example, the assessment $p_{\rm dice}(\{1\}) = 1/6$, is based on the knowledge that there are six possible outcomes to a dice throw, and that in the absence of any prior reason to believe that the dice is biased, all six are equally likely. All assignments of probability in Statistical Mechanics are subjectively based.The consequences of such subjective assignments of probability have to be checked against measurements, and they may need to be modified as more information about the outcomes becomes available.

II.B One Random Variable

As the properties of a discrete random variable are rather well known, here we focus on continuous random variables, which are more relevant to our purposes. Consider a random variable x, whose outcomes are real numbers, i.e. $\mathcal{S}_x = \{-\infty < x < \infty\}$.

• *The cumulative probability function* (CPF) $P(x)$, is the probability of an outcome with *any value* less than x, i.e. $P(x) = \text{prob.}(E \subset [-\infty, x])$. $P(x)$ must be a monotonically increasing function of x, with $P(-\infty) = 0$ and $P(+\infty) = 1$.

• *The probability density function* (PDF) is defined by $p(x) \equiv dP(x)/dx$. Hence, $p(x)dx = \text{prob.}(E \subset [x, x + dx])$. As a probability density, it is *positive*, and normalized such that

$$\text{prob.}(\mathcal{S}) = \int_{-\infty}^{\infty} dx\ p(x) = 1\ . \tag{II.1}$$

Note that since $p(x)$ is a *probability density*, it has no upper bound, i.e. $0 < p(x) < \infty$.

• *The expectation value* of any function $F(x)$, of the random variable is

$$\langle F(x) \rangle = \int_{-\infty}^{\infty} dx\ p(x)F(x)\ . \tag{II.2}$$

The function $F(x)$ is itself a random variable, with an associated PDF of $p_F(f)df = \text{prob.}(F(x) \subset [f, f + df])$. There may be multiple solutions x_i, to the equation $F(x) = f$, and

$$p_F(f)df = \sum_i p(x_i)dx_i\,, \quad \Longrightarrow \quad p_F(f) = \sum_i p(x_i) \left| \frac{dx}{dF} \right|_{x=x_i} \ . \tag{II.3}$$

The factors of $|dx/dF|$ are the *Jacobians* associated with the change of variables from x to F. For example, consider $p(x) = \lambda \exp(-\lambda|x|)/2$, and the function $F(x) = x^2$. There are two solutions to $F(x) = f$, located at $x_\pm = \pm\sqrt{f}$, with corresponding Jacobians $| \pm f^{-1/2}/2|$. Hence,

$$P_F(f) = \frac{\lambda}{2} \exp\left(-\lambda\sqrt{f}\right) \left(\left| \frac{1}{2\sqrt{f}} \right| + \left| \frac{-1}{2\sqrt{f}} \right| \right) = \frac{\lambda \exp\left(-\lambda\sqrt{f}\right)}{2\sqrt{f}} \,,$$

for $f > 0$, and $p_F(f) = 0$ for $f < 0$. Note that $p_F(f)$ has an (integrable) divergence at $f = 0$.

• *Moments* of the PDF are expectation values for powers of the random variable. The n^{th} moment is

$$m_n \equiv \langle x^n \rangle = \int dx p(x)\ x^n. \tag{II.4}$$

• *The characteristic function*, is the generator of moments of the distribution. It is simply the Fourier transform of the PDF, defined by

$$\tilde{p}(k) = \left\langle e^{-ikx} \right\rangle = \int dx p(x)\ e^{-ikx}. \tag{II.5}$$

The PDF can be recovered from the characteristic function through the inverse Fourier transform

$$p(x) = \frac{1}{2\pi} \int dk \tilde{p}(k)\ e^{+ikx}. \tag{II.6}$$

Moments of the distribution are obtained by expanding $\tilde{p}(k)$ in powers of k,

$$\tilde{p}(k) = \left\langle \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} x^n \right\rangle = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle \quad . \tag{II.7}$$

Moments of the PDF around any point x_0 can also be generated by expanding

$$e^{ikx_0} \tilde{p}(k) = \left\langle e^{-ik(x-x_0)} \right\rangle = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle (x - x_0)^n \rangle \quad . \tag{II.8}$$

• *The cumulant generating function* is the logarithm of the characteristic function. Its expansion generates the *cumulants* of the distribution defined through

$$\ln \tilde{p}(k) = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle_c \quad . \tag{II.9}$$

Relations between moments and cumulants can be obtained by expanding the logarithm of $\tilde{p}(k)$ in eq.(II.7), and using

$$\ln(1+\epsilon) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\epsilon^n}{n} \quad . \tag{II.10}$$

The first four cumulants are called the *mean*, *variance*, *skewness*, and *curtosis* of the distribution respectively, and are obtained from the moments as

$$\begin{aligned}
\langle x \rangle_c &= \langle x \rangle \,, \\
\left\langle x^2 \right\rangle_c &= \left\langle x^2 \right\rangle - \langle x \rangle^2 \,, \\
\left\langle x^3 \right\rangle_c &= \left\langle x^3 \right\rangle - 3 \left\langle x^2 \right\rangle \langle x \rangle + 2 \langle x \rangle^3 \,, \\
\left\langle x^4 \right\rangle_c &= \left\langle x^4 \right\rangle - 4 \left\langle x^3 \right\rangle \langle x \rangle - 3 \left\langle x^2 \right\rangle^2 + 12 \left\langle x^2 \right\rangle \langle x \rangle^2 - 6 \langle x \rangle^4 \,.
\end{aligned} \tag{II.11}$$

The cumulants provide a useful and compact way of describing a PDF.

An important theorem allows easy computation of moments in terms of the cumulants: Represent the n^{th} cumulant graphically as a *connected cluster* of n points. The m^{th} moment is then obtained by summing all possible subdivisions of m points into groupings of smaller (connected or disconnected) clusters. The contribution of each subdivision to the sum is the product of the connected cumulants that it represents. Using this result the first four moments are easily computed as

$$\begin{aligned}
\langle x \rangle &= \langle x \rangle_c \,, \\
\left\langle x^2 \right\rangle &= \left\langle x^2 \right\rangle_c + \langle x \rangle_c^2 \,, \\
\left\langle x^3 \right\rangle &= \left\langle x^3 \right\rangle_c + 3 \left\langle x^2 \right\rangle_c \langle x \rangle_c + \langle x \rangle_c^3 \,, \\
\left\langle x^4 \right\rangle &= \left\langle x^4 \right\rangle_c + 4 \left\langle x^3 \right\rangle_c \langle x \rangle_c + 3 \left\langle x^2 \right\rangle_c^2 + 6 \left\langle x^2 \right\rangle_c \langle x \rangle_c^2 + \langle x \rangle_c^4 \,.
\end{aligned} \tag{II.12}$$

This theorem, which is the starting point for various diagrammatic computations is statistical mechanics and field theory, is easily proved by equating the expression in eqs. (II.7) and (II.9) for $\tilde{p}(k)$

$$\sum_{m=0}^{\infty} \frac{(-ik)^m}{m!} \langle x^m \rangle = \exp\left[\sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle_c \right] = \prod_n \sum_{p_n} \left[\frac{(-ik)^{np_n}}{p_n!} \left(\frac{\langle x^n \rangle_c}{n!} \right)^{p_n} \right] . \tag{II.13}$$

Equating the powers of $(-ik)^m$ on the two sides of the above expression leads to

$$\langle x^m \rangle = {\sum_{\{p_n\}}}' \prod_n \frac{m!}{p_n! (n!)^{p_n}} \langle x^n \rangle_c^{p_n} \,. \tag{II.14}$$

The sum is restricted such that $\sum n p_n = m$, and leads to the graphical interpretation given above, as the numerical factor is simply the number of ways of breaking m points into $\{p_n\}$ clusters of n points.

II.C Some Important Probability Distributions

The properties of three commonly encountered probability distributions are examined in this section.

(1) *The normal (Gaussian) distribution* describes a continuous real random variable x, with

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(x-\lambda)^2}{2\sigma^2}\right] \quad . \tag{II.15}$$

The corresponding characteristic function also has a Gaussian form,

$$\tilde{p}(k) = \int_{-\infty}^{\infty} dx \; \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(x-\lambda)^2}{2\sigma^2} - ikx\right] = \exp\left[-ik\lambda - \frac{k^2\sigma^2}{2}\right] \quad . \tag{II.16}$$

Cumulants of the distribution can be identified from $\ln \tilde{p}(k) = -ik\lambda - k^2\sigma^2/2$, using eq.(II.9), as

$$\langle x \rangle_c = \lambda \quad , \quad \langle x^2 \rangle_c = \sigma^2 \quad , \quad \langle x^3 \rangle_c = \langle x^4 \rangle_c = \cdots = 0 \quad . \tag{II.17}$$

The normal distribution is thus completely specified by its two first cumulants. This makes the computation of moments using the cluster expansion (eqs.(II.12)) particularly simple, and

$$\begin{aligned} \langle x \rangle &= \lambda \,, \\ \langle x^2 \rangle &= \sigma^2 + \lambda^2, \\ \langle x^3 \rangle &= 3\sigma^2\lambda + \lambda^3, \\ \langle x^4 \rangle &= 3\sigma^4 + 6\sigma^2\lambda^2 + \lambda^4, \quad \cdots \quad . \end{aligned} \tag{II.18}$$

The normal distribution serves as the starting point for most perturbative computations in field theory. The vanishing of higher cumulants implies that all graphical computations involve only products of one point, and two point (known as propagators) clusters.

(2) *The binomial distribution:* Consider a random variable with two outcomes A and B (e.g. a coin toss) of relative probabilities p_A and $p_B = 1 - p_A$. The probability that in N trials the event A occurs exactly N_A times (e.g. 5 heads in 12 coin tosses), is given by the binomial distribution

$$p_N(N_A) = \binom{N}{N_A} p_A^{N_A} p_B^{N-N_A} \; . \tag{II.19}$$

The prefactor,

$$\binom{N}{N_A} = \frac{N!}{N_A!(N-N_A)!} \; , \tag{II.20}$$

is just the coefficient obtained in the binomial expansion of $(p_A+p_B)^N$, and gives the number of possible orderings of N_A events A and $N_B = N - N_A$ events B. The characteristic function for this discrete distribution is given by

$$\tilde{p}_N(k) = \left\langle e^{-ikN_A} \right\rangle = \sum_{N_A=0}^{N} \frac{N!}{N_A!(N-N_A)!}\, p_A^{N_A} p_B^{N-N_A}\, e^{-ikN_A} = \left(p_A e^{-ik} + p_B\right)^N \quad . \tag{II.21}$$

The resulting cumulant generating function is

$$\ln \tilde{p}_N(k) = N \ln\left(p_A e^{-ik} + p_B\right) = N \ln \tilde{p}_1(k), \tag{II.22}$$

where $\ln \tilde{p}_1(k)$ is the cumulant generating function for a single trial. Hence, the cumulants after N trials are simply N times the cumulants in a single trial. In each trial, the allowed values of N_A are 0 and 1 with respective probabilities p_B and p_A, leading to $\left\langle N_A^\ell \right\rangle = p_A$, for all ℓ. After N trials the first two cumulants are

$$\langle N_A \rangle_c = N p_A \quad , \quad \left\langle N_A^2 \right\rangle_c = N(p_A - p_A^2) = N p_A p_B \quad . \tag{II.23}$$

A measure of fluctuations around the mean is provided by the *standard deviation*, which is the square root of the variance. While the mean of the binomial distribution scales as N, its standard deviation only grows as $\sqrt{N}$. Hence, the *relative* uncertainty becomes smaller for large N.

The binomial distribution is straightforwardly generalized to a *multinomial* distribution, when the several outcomes $\{A, B, \cdots, M\}$ occur with probabilities $\{p_A, p_B, \cdots, p_M\}$. The probability of finding outcomes $\{N_A, N_B, \cdots, N_M\}$ in a total of $N = N_A + N_B \cdots + N_M$ trials is

$$p_N\left(\{N_A, N_B, \cdots, N_M\}\right) = \frac{N!}{N_A! N_B! \cdots N_M!} p_A^{N_A} p_B^{N_B} \cdots p_M^{N_M} \quad . \tag{II.24}$$

(3) *The Poisson distribution:* The classical example of a Poisson process is radioactive decay. Observing a piece of radioactive material over a time interval T shows that:

(a) The probability of one and only one event (decay) in the interval $[t, t+dt]$ is proportional to dt as $dt \to 0$,

(b) The probabilities of events at different intervals are independent of each other.

The probability of observing exactly M decays in the interval T is given by the Poisson distribution. It is obtained as a limit of the binomial distribution by subdividing the interval into $N = T/dt \gg 1$ segments of size dt. In each segment, an event occurs with probability $p = \alpha dt$, and there is no event with probability $q = 1 - \alpha dt$. As the probability

of more than one event in dt is too small to consider, the process is equivalent to a binomial one. Using eq.(II.21), the characteristic function is given by

$$\tilde{p}(k) = \left(pe^{-ik} + q\right)^n = \lim_{dt\to 0} \left[1 + \alpha dt \left(e^{-ik} - 1\right)\right]^{T/dt} = \exp\left[\alpha(e^{-ik} - 1)T\right] \quad . \tag{II.25}$$

The Poisson PDF is obtained from the inverse Fourier transform in eq.(II.6) as

$$p(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp\left[\alpha\left(e^{-ik} - 1\right)T + ikx\right] = e^{-\alpha T} \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ikx} \sum_{M=0}^{\infty} \frac{(\alpha T)^M}{M!} e^{-ikM} \ , \tag{II.26}$$

using the power series for the exponential. The integral over k is

$$\int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ik(x-M)} = \delta(x - M) \ , \tag{II.27}$$

leading to

$$p_{\alpha T}(x) = \sum_{m=0}^{\infty} e^{-\alpha T} \ \frac{(\alpha T)^M}{M!} \delta(x - M) \ . \tag{II.28}$$

The probability of M events is thus $p_{\alpha T}(M) = e^{-\alpha T}(\alpha T)^M/M!$. The cumulants of the distribution are obtained from the expansion

$$\ln \tilde{p}_{\alpha T}(k) = \alpha T(e^{-ik} - 1) = \alpha T \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!}, \quad \Longrightarrow \quad \langle M^n \rangle_c = \alpha T \quad . \tag{II.29}$$

All cumulants have the same value, and the moments are obtained from eqs.(II.12) as

$$\langle M \rangle = (\alpha T), \quad \left\langle M^2 \right\rangle = (\alpha T)^2 + (\alpha T), \quad \left\langle M^3 \right\rangle = (\alpha T)^3 + 3(\alpha T)^2 + (\alpha T). \tag{II.30}$$

Example: Assuming that stars are randomly distributed in the galaxy (clearly unjustified) with a density n, what is the probability that the nearest star is at a distance R?

Since, the probability of finding a star in a small volume dV is ndV, and they are assumed to be independent, the number of stars in a volume V is described by a Poisson process as in eq.(II.28), with $\alpha = n$. The probability $p(R)$, of encountering the first star at a distance R is the product of the probabilities $p_{nV}(0)$, of finding zero stars in the volume $V = 4\pi R^3/3$ around the origin, and $p_{ndV}(1)$, of finding one star in the shell of volume $dV = 4\pi R^2 dR$ at a distance R. Both $p_{nV}(0)$ and $p_{ndV}(1)$ can be calculated from eq.(II.28), and

$$\begin{aligned} p(R)dR = p_{nV}(0)\, p_{ndV}(1) =& e^{-4\pi R^3 n/3}\, e^{-4\pi R^2 ndR}\, 4\pi R^2 ndR, \\ \Longrightarrow \qquad p(R) =& 4\pi R^2 n \exp\left(-\frac{4\pi}{3} R^3 n\right) \ . \end{aligned} \tag{II.31}$$

II.D Many Random Variables

With more than one random variable, the set of outcomes is an N-dimensional space, $\mathcal{S}_{\mathbf{x}} = \{-\infty < x_1, x_2, \cdots, x_N < \infty\}$. For example, describing the location and velocity of a gas particle requires six coordinates.

• *The joint PDF* $p(\mathbf{x})$, is the probability density of an outcome in a volume element $d^N\mathbf{x} = \prod_{i=1}^{N} dx_i$ around the point $\mathbf{x} = \{x_1, x_2, \cdots, x_N\}$. The joint PDF is normalized such that

$$p_{\mathbf{x}}(\mathcal{S}) = \int d^N\mathbf{x}\; p(\mathbf{x}) = 1 \; . \tag{II.32}$$

If, and only if, the N random variables are *independent*, the joint PDF is the product of individual PDFs,

$$p(\mathbf{x}) = \prod_{i=1}^{N} p_i(x_i) \quad . \tag{II.33}$$

• *The unconditional PDF* describes the behavior of a subset of random variables, independent of the values of the others. For example, if we are interested only in the location of a gas particle, an unconditional PDF can be constructed by integrating over all velocities at a given location, $p(\vec{x}) = \int d^3\vec{v}\; p(\vec{x}, \vec{v})$; more generally

$$p(x_1, \cdots, x_m) = \int \prod_{i=m+1}^{N} dx_i \; p(x_1, \cdots, x_N) \; . \tag{II.34}$$

• *The conditional PDF* describes the behavior of a subset of random variables, for specified values of the others. For example, the PDF for the velocity of a particle at a particular location $\vec{x}$, denoted by $p(\vec{v} \mid \vec{x})$, is proportional to the joint PDF $p(\vec{v} \mid \vec{x}) = p(\vec{x}, \vec{v})/\mathcal{N}$. The constant of proportionality, obtained by normalizing $p(\vec{v} \mid \vec{x})$, is

$$\mathcal{N} = \int d^3\vec{v}\; p(\vec{x}, \vec{v}) = p(\vec{x}), \tag{II.35}$$

the unconditional PDF for a particle at $\vec{x}$. In general, the unconditional PDFs are obtained from *Bayes' Theorem* as

$$p(x_1, \cdots, x_m \mid x_{m+1}, \cdots, x_N) = \frac{p(x_1, \cdots, x_N)}{p(x_{m+1}, \cdots, x_N)} \quad . \tag{II.36}$$

Note that if the random variables are independent, the unconditional PDF is equal to the conditional PDF.

• *The expectation value* of a function $F(\mathbf{x})$, is obtained as before from

$$\langle F(\mathbf{x})\rangle = \int d^N\mathbf{x}\; p(\mathbf{x})F(\mathbf{x}) \; . \tag{II.37}$$

• *The joint characteristic function*, is obtained from the N-dimensional Fourier transformation of the joint PDF,

$$\tilde{p}(\mathbf{k}) = \left\langle \exp\left(-i\sum_{j=1}^{N} k_j x_j\right)\right\rangle \quad . \tag{II.38}$$

The *joint moments* and *joint cumulants* are generated by $\tilde{p}(\mathbf{k})$ and $\ln\tilde{p}(\mathbf{k})$ respectively, as

$$\begin{aligned} \langle x_1^{n_1}x_2^{n_2}\cdots x_N^{n_N}\rangle &= \left[\frac{\partial}{\partial(-ik_1)}\right]^{n_1}\left[\frac{\partial}{\partial(-ik_2)}\right]^{n_2}\cdots\left[\frac{\partial}{\partial(-ik_N)}\right]^{n_N}\tilde{p}(\mathbf{k}=\mathbf{0}) \quad , \\ \langle x_1^{n_1}x_2^{n_2}\cdots x_N^{n_N}\rangle_c &= \left[\frac{\partial}{\partial(-ik_1)}\right]^{n_1}\left[\frac{\partial}{\partial(-ik_2)}\right]^{n_2}\cdots\left[\frac{\partial}{\partial(-ik_N)}\right]^{n_N}\ln\tilde{p}(\mathbf{k}=\mathbf{0}) \quad . \end{aligned} \tag{II.39}$$

The previously described graphical relation between joint moments (all clusters of labelled points), and joint cumulant (connected clusters) is still applicable. For example

$$\begin{aligned} \langle x_\alpha x_\beta\rangle &= \langle x_\alpha\rangle_c\langle x_\beta\rangle_c + \langle x_\alpha x_\beta\rangle_c \quad , \quad \text{and} \\ \langle x_\alpha^2 x_\beta\rangle &= \langle x_\alpha\rangle_c^2\langle x_\beta\rangle_c + \langle x_\alpha^2\rangle_c\langle x_\beta\rangle_c + 2\langle x_\alpha x_\beta\rangle_c\langle x_\alpha\rangle_c + \langle x_\alpha^2 x_\beta\rangle_c \quad . \end{aligned} \tag{II.40}$$

The *connected correlation*, $\langle x_\alpha x_\beta\rangle_c$, is zero if x_α and x_β are independent random variables.

• *The joint Gaussian distribution* is the generalization of eq.(II.15) to N random variables, as

$$p(\mathbf{x}) = \frac{1}{\sqrt{(2\pi)^N\det[C]}}\exp\left[-\frac{1}{2}\sum_{mn}\left(C^{-1}\right)_{mn}(x_m-\lambda_m)(x_n-\lambda_n)\right] \quad , \tag{II.41}$$

where C is a symmetric matrix, and C^{-1} is its inverse,. The simplest way to get the normalization factor is to make a linear transformation from the variables $y_j = x_j - \lambda_j$, using the unitary matrix that diagonalizes C. This reduces the normalization to that of the product of N Gaussians whose variances are determined by the eigenvalues of C. The product of the eigenvalues is the determinant $\det[C]$. (This also indicates that the matrix C must be positive definite.) The corresponding joint characteristic function is obtained by similar manipulations, and is given by

$$\tilde{p}(\mathbf{k}) = \exp\left[-ik_m\lambda_m - \frac{1}{2}C_{mn}k_mk_n\right] \quad , \tag{II.42}$$

where the summation convention is used.

The joint cumulants of the Gaussian are then obtained from $\ln \tilde{p}(\mathbf{k})$ as

$$\langle x_m \rangle_c = \lambda_m \quad , \quad \langle x_m x_n \rangle_c = C_{mn} \quad , \tag{II.43}$$

with all higher cumulants equal to zero. In the special case of $\{\lambda_m\} = 0$, all odd *moments* of the distribution are zero, while the general rules for relating moments to cumulants indicate that any even moment is obtained by summing over all ways of grouping the involved random variables into pairs, e.g.

$$\langle x_a x_b x_c x_d \rangle = C_{ab}C_{cd} + C_{ac}C_{bd} + C_{ad}C_{bc}. \tag{II.44}$$

This result is sometimes referred to as *Wick's theorem*.

II.E Sums of Random Variables & the Central Limit Theorem

Consider the sum $X = \sum_{i=1}^{N} x_i$, where x_i are random variables with a joint PDF of $p(\mathbf{x})$. The PDF for X is

$$p_X(x) = \int d^N\mathbf{x}\; p(\mathbf{x}) \delta\left(x - \sum x_i\right) = \int \prod_{i=1}^{N-1} dx_i \; p\left(x_1, \cdots, x_{N-1}, x - x_1 \cdots - x_{N-1}\right), \tag{II.45}$$

and the corresponding characteristic function (using eq.(II.38)) is given by

$$\tilde{p}_X(k) = \left\langle \exp\left(-ik \sum_{j=1}^{N} x_j\right) \right\rangle = \tilde{p}\left(k_1 = k_2 = \cdots = k_N = k\right). \tag{II.46}$$

Cumulants of the sum are obtained by expanding $\ln \tilde{p}_X(k)$,

$$\ln \tilde{p}\left(k_1 = k_2 = \cdots = k_N = k\right) = -ik \sum_{i_1=1}^{N} \langle x_{i_1} \rangle_c + \frac{(-ik)^2}{2} \sum_{i_1, i_2}^{N} \langle x_{i_1} x_{i_2} \rangle_c + \cdots, \tag{II.47}$$

as

$$\langle X \rangle_c = \sum_{i=1}^{N} \langle x_i \rangle_c \quad , \quad \langle X^2 \rangle_c = \sum_{i,j}^{N} \langle x_i x_j \rangle_c \quad , \quad \cdots. \tag{II.48}$$

If the random variables are independent, $p(\mathbf{x}) = \prod p_i(x_i)$, and $\tilde{p}_X(k) = \prod \tilde{p}_i(k)$. The cross–cumulants in eq.(II.48) vanish, and the n^{th} cumulant of X is simply the sum of the individual cumulants, $\langle X^n \rangle_c = \sum_{i=1}^{N} \langle x_i^n \rangle_c$. When all the N random variables

are independently taken from the same distribution $p(x)$, this implies $\langle X^n \rangle_c = N \langle x^n \rangle_c$, generalizing the result obtained previously for the binomial distribution. For large values of N, the average value of the sum is proportional to N, while fluctuations around the mean, as measured by the standard deviation, grow only as $\sqrt{N}$. The random variable $y = (X - N \langle x \rangle_c)/\sqrt{N}$, has zero mean, and cumulants that scale as $\langle y^n \rangle_c \propto N^{1-m/2}$. As $N \to \infty$, only the second cumulant survives, and the PDF for y converges to the normal distribution ,

$$\lim_{N\to\infty} p\left(y = \frac{\sum_{i=1}^{N} x_i - N \langle x \rangle_c}{\sqrt{N}} \right) = \frac{1}{\sqrt{2\pi \langle x^2 \rangle_c}} \exp\left(-\frac{y^2}{2 \langle x^2 \rangle_c} \right). \tag{II.49}$$

(Note that the Gaussian distribution is the only distribution with only first and second cumulants.)

The convergence of the PDF for the sum of many random variables to a normal distribution is a most important result in the context of statistical mechanics where such sums are frequently encountered. The *central limit theorem* states a more general form of this result: It is not necessary for the random variables to be independent, as the condition $\sum_{i_1,\cdots,i_m}^{N} \langle x_{i_1} \cdots x_{i_m} \rangle_c \ll \mathcal{O}(N^{m/2})$, is sufficient for the validity of eq.(II.49).

II.F Rules for Large Numbers

To describe equilibrium properties of macroscopic bodies, statistical mechanics has to deal with the very large number N, of microscopic degrees of freedom. Actually, taking the *thermodynamic limit* of $N \to \infty$ leads to a number of simplifications, some of which are described in this section.

There are typically three types of N dependence encountered in the thermodynamic limit:

(a) *Intensive* quantities, such as temperature T, and generalized forces, e.g. pressure P, and magnetic field $\vec{B}$, are independent of N, i.e. $\mathcal{O}(N^0)$.

(b) *Extensive* quantities, such as energy E, entropy S, and generalized displacements, e.g. volume V, and magnetization $\vec{M}$, are proportional to N, i.e. $\mathcal{O}(N^1)$.

(c) *Exponential* dependence, i.e. $\mathcal{O}\big(\exp(N\phi)\big)$, is encountered in enumerating discrete micro-states, or computing available volumes in phase space.

Other asymptotic dependencies are certainly not ruled out a priori. For example, the Coulomb energy of N ions at fixed density scales as $Q^2/R \sim N^{5/3}$. Such dependencies are rarely encountered in every day physics. The Coulomb interaction of ions is quickly

screened by counter-ions, resulting in an extensive overall energy. (This is not the case in astrophysical problems since the gravitational energy can not be screened. For example the entropy of a black hole is proportional to the square of its mass.)

In statistical mechanics we frequently encounter sums or integrals of exponential variables. Performing such sums in the thermodynamic limit is considerably simplified due to the following results.

(1) *Summation of Exponential Quantities*

Consider the sum

$$\mathcal{S} = \sum_{i=1}^{\mathcal{N}} \mathcal{E}_i \quad , \tag{II.50}$$

where each term is positive, with an exponential dependence on N,

$$0 \leq \mathcal{E}_i \sim \mathcal{O}\big(\exp(N\phi_i)\big), \tag{II.51}$$

and the number of terms $\mathcal{N}$, is proportional to some power of N. Such a sum can be approximated by its largest term $\mathcal{E}_{\max}$, in the following sense. Since for each term in the sum, $0 \leq \mathcal{E}_i \leq \mathcal{E}_{\max}$,

$$\mathcal{E}_{\max} \leq \mathcal{S} \leq \mathcal{N}\mathcal{E}_{\max} \ . \tag{II.52}$$

An intensive quantity can be constructed from $\ln \mathcal{S}/N$, which is bounded by

$$\frac{\ln \mathcal{E}_{\max}}{N} \leq \frac{\ln \mathcal{S}}{N} \leq \frac{\ln \mathcal{E}_{\max}}{N} + \frac{\ln \mathcal{N}}{N} \ . \tag{II.53}$$

For $\mathcal{N} \propto N^p$, the ratio $\ln \mathcal{N}/N$ vanishes in the large N limit, and

$$\lim_{N\to\infty} \frac{\ln \mathcal{S}}{N} = \frac{\ln \mathcal{E}_{\max}}{N} = \phi_{\max} \quad . \tag{II.54}$$

(2) *Saddle Point Integration*

Similarly, an integral of the form

$$\mathcal{I} = \int dx \exp\big(N\phi(x)\big) \quad , \tag{II.55}$$

can be approximated by the maximum value of the integrand, obtained at a point $x_{\max}$ which maximizes the exponent $\phi(x)$. Expanding around this point,

$$\mathcal{I} = \int dx \exp\left\{ N\left[\phi(x_{\max}) - \frac{1}{2}|\phi''(x_{\max})|(x - x_{\max})^2 + \cdots \right] \right\}. \tag{II.56}$$

Note that at the maximum, the first derivative $\phi'(x_{\max})$, is zero, while the second derivative $\phi''(x_{\max})$, is negative. Terminating the series at the quadratic order results in

$$\mathcal{I} \approx e^{N\phi(x_{\max})} \int dx \exp\left[-\frac{N}{2}|\phi''(x_{\max})|(x-x_{\max})^2\right] \approx \sqrt{\frac{2\pi}{N|\phi''(x_{\max})|}} e^{N\phi(x_{\max})}, \quad \text{(II.57)}$$

where the range of integration has been extended to $[-\infty,\infty]$. The latter is justified since the integrand is negligibly small outside the neighborhood of $x_{\max}$.

There are two types of correction to the above result. Firstly, there are higher order terms in the expansion of $\phi(x)$ around $x_{\max}$. These corrections can be looked at perturbatively, and lead to a series in powers of $1/N$. Secondly, there may be additional local maxima for the function. A maximum at $x'_{\max}$, leads to a similar Gaussian integral that can be added to eq.(II.57). Clearly such contributions are smaller by $\mathcal{O}\big(\exp\{-N[\phi(x_{\max})-\phi(x'_{\max})]\}\big)$. Since all these corrections vanish in the thermodynamic limit,

$$\lim_{N\to\infty} \frac{\ln \mathcal{I}}{N} = \lim_{N\to\infty} \left[\phi(x_{\max}) - \frac{1}{2N}\ln\big(\frac{N|\phi''(x_{\max})|}{2\pi}\big) + \mathcal{O}(\frac{1}{N^2})\right] = \phi(x_{\max}) \quad . \quad \text{(II.58)}$$

The *saddle point* method for evaluating integrals is the extension of the above result to more general integrands, and integration paths in the complex plane. (The appropriate extremum in the complex plane is a saddle point.) The simplified version presented above is sufficient for the purposes of this course.

• *Stirling's approximation* for $N!$ at large N can be obtained by saddle point integration. In order to get an integral representation of $N!$, start with the result

$$\int_0^\infty dx e^{-\alpha x} = \frac{1}{\alpha}. \quad \text{(II.59)}$$

Repeated differentiation of both sides of the above equation with respect to α leads to

$$\int_0^\infty dx x^N e^{-\alpha x} = \frac{N!}{\alpha^{N+1}}. \quad \text{(II.60)}$$

Although the above result only applies to integer N, it is possible to define by analytical continuation a function,

$$\Gamma(N+1) \equiv N! = \int_0^\infty dx x^N e^{-x}, \quad \text{(II.61)}$$

for all N. While the integral in eq.(II.61) is not exactly in the form of eq.(II.55), it can still be evaluated by a similar method. The integrand can be written as $\exp\big(N\phi(x)\big)$, with $\phi(x) = \ln x - x/N$. The exponent has a maximum at $x_{\max} = N$, with $\phi(x_{\max}) = \ln N - 1$, and $\phi''(x_{\max}) = -1/N^2$. Expanding the integrand in eq.(II.61) around this point yields,

$$N! \approx \int dx \exp\big(N \ln N - N - \frac{1}{2N}(x-N)^2\big) \approx N^N e^{-N}\sqrt{2\pi N}, \tag{II.62}$$

where the integral is evaluated by extending its limits to $[-\infty, \infty]$. Stirling's formula is obtained by taking the logarithm of eq.(II.62) as,

$$\ln N! = N \ln N - N + \frac{1}{2}\ln(2\pi N) + \mathcal{O}(\frac{1}{N}). \tag{II.63}$$

II.G Information, Entropy, and Estimation

• *Information:* Consider a random variable with a discrete set of outcomes $\mathcal{S} = \{x_i\}$, occurring with probabilities $\{p(i)\}$, for $i = 1, \cdots, M$. In the context of information theory, there is a precise meaning to the *information content* of a probability distribution: Let us construct a message from N independent outcomes of the random variable. Since there are M possibilities for each character in this message, it has an apparent information content of $N \ln_2 M$ bits; i.e. this many binary bits of information have to be transmitted to convey the message precisely. On the other hand, the probabilities $\{p(i)\}$ limit the types of messages that are likely. For example, if $p_2 \gg p_1$, it is very unlikely to construct a message with more x_1 than x_2. In particular, in the limit of large N, we expect the message to contain "roughly" $\{N_i = Np_i\}$ occurrences of each symbol.† The number of typical messages thus corresponds to the number of ways of rearranging the $\{N_i\}$ occurrences of $\{x_i\}$, and is given by the multinomial coefficient

$$g = \frac{N!}{\prod_{i=1}^{M} N_i!}. \tag{II.64}$$

This is much smaller than the total number of messages M^n. To specify one out of g possible sequences requires

$$\ln_2 g \approx -N \sum_{i=1}^{M} p_i \ln_2 p_i \qquad (\text{for } N \to \infty), \tag{II.65}$$

† More precisely, the probability of finding any N_i that is different from Np_i by more than $\pm\sqrt{N}$ becomes exponentially small in N, as $N \to \infty$.

bits of information. The last result is obtained by applying Stirling's approximation for $\ln N!$. It can also be obtained by noting that

$$1 = \left(\sum_i p_i \right)^N = \sum_{\{N_i\}} N! \prod_{i=1}^{M} \frac{p_i^{N_i}}{N_i!} \approx g \prod_{i=1}^{M} p_i^{N p_i}, \tag{II.66}$$

where the sum has been replaced by its largest term, as justified in the previous section.

Shannon's Theorem proves more rigorously that the minimum number of bits necessary to ensure that the percentage of errors in N trials vanishes in the $N \to \infty$ limit, is $\ln_2 g$. For any non-uniform distribution, this is less than the $N \ln_2 M$ bits needed in the absence of any information on relative probabilities. The difference per trial is thus attributed to the information content of the probability distribution, and is given by

$$I\left[\{p_i\}\right] = \ln_2 M + \sum_{i=1}^{M} p_i \ln_2 p_i \quad . \tag{II.67}$$

• *Entropy:* Eq.(II.64) is encountered frequently in statistical mechanics in the context of mixing M distinct components; its natural logarithm is related to the *entropy of mixing.* More generally, we can define an *entropy* for *any probability distribution* as

$$S = -\sum_{i=1}^{M} p(i) \ln p(i) = -\left\langle \ln p(i) \right\rangle \quad . \tag{II.68}$$

The above entropy takes a minimum value of zero for the delta–function distribution $p(i) = \delta_{i,j}$, and a maximum value of $\ln M$ for the uniform distribution, $p(i) = 1/M$. S is thus a measure of dispersity (disorder) of the distribution, and does not depend on the values of the random variables $\{x_i\}$. A one to one mapping to $f_i = F(x_i)$ leaves the entropy unchanged, while a many to one mapping makes the distribution more ordered and decrease S. For example, if the two values, x_1 and x_2, are mapped onto the same f, the change in entropy is

$$\Delta S(x_1, x_2 \to f) = \left[p_1 \ln \frac{p_1}{p_1 + p_2} + p_2 \ln \frac{p_2}{p_1 + p_2} \right] < 0. \tag{II.69}$$

• *Estimation:* The entropy S, can also be used to quantify subjective estimates of probabilities. In the absence of any information, the best *unbiased estimate* is that all M outcomes are equally likely. This is the distribution of maximum entropy. If additional information is available, the unbiased estimate is obtained by maximizing the entropy subject to the

constraints imposed by this information. For example, if it is known that $\langle F(x)\rangle = f$, we can maximize

$$S\left(\alpha,\beta,\{p_i\}\right) = -\sum_i p(i)\ln p(i) - \alpha\left(\sum_i p(i) - 1\right) - \beta\left(\sum_i p(i)F(x_i) - f\right), \quad \text{(II.70)}$$

where the Lagrange multipliers α and β are introduced to impose the constraints of normalization, and $\langle F(x)\rangle = f$, respectively. The result of the optimization is a distribution $p_i \propto \exp\big(-\beta F(x_i)\big)$, where the value of β is fixed by the constraint. This process can be generalized to an arbitrary number of conditions. It is easy to see that if the first n moments (and hence n cumulants) of a distribution are specified, the unbiased estimate is the exponential of an n^{th} order polynomial.

In analogy with eq.(II.68), we can define an entropy for a continuous random variable ($\mathcal{S}_x = \{-\infty < x < \infty\}$) as

$$S = -\int dx\, p(x)\ \ln p(x) = -\left\langle \ln p(x)\right\rangle \quad . \quad \text{(II.71)}$$

There are, however, problems with this definition, as for example S is not invariant under a one to one mapping. (After a change of variable to $f = F(x)$, the entropy is changed by $\langle |F'(x)|\rangle$.) Since the Jacobian of a canonical transformation is unity, canonically conjugate pairs offer a suitable choice of coordinates in classical statistical mechanics. The ambiguities are also removed if the continuous variable is discretized. This happens quite naturally in quantum statistical mechanics where it is usually possible to work with a discrete ladder of states. The appropriate volume for discretization of phase space is set by Planck's constant $\hbar$.

III. Kinetic Theory of Gases

III.A General Definitions

• **Kinetic theory** *studies the macroscopic properties of large numbers of particles, starting from their (classical) equations of motion.*

Thermodynamics describes the equilibrium behavior of *macroscopic objects* in terms of concepts such as work, heat, and entropy. The phenomenological laws of thermodynamics tell us how these quantities are constrained as a system approaches its equilibrium. At the *microscopic level*, we know that these systems are composed of particles (atoms, molecules), whose interactions and dynamics are reasonably well understood in terms of more fundamental theories. If these microscopic descriptions are complete, we should be able to account for the macroscopic behavior, i.e. derive the laws governing the macroscopic state functions in equilibrium. Kinetic theory attempts to achieve this objective. In particular, we shall try to answer the following questions:

(1) How can we define "equilibrium" for a system of moving particles?

(2) Do all systems naturally evolve towards an equilibrium state?

(3) What is the time evolution of a system that is not quite in equilibrium?

The simplest system to study, the veritable work–horse of thermodynamics, is the dilute (nearly ideal) gas. A typical volume of gas contains of the order of 10^{23} particles. Kinetic theory attempts to deduce the macroscopic properties of the gas from the time evolution of the individual atomic coordinates. At any time t, the *microstate* of a system of N particles is described by specifying the positions $\vec{q}_i(t)$, and momenta $\vec{p}_i(t)$, of all particles. The microstate thus corresponds to a point $\mu(t)$, in the $6N$ dimensional *phase space* $\Gamma = \prod_{i=1}^{N}\{\vec{q}_i, \vec{p}_i\}$. The time evolution of this point is governed by the canonical equations

$$\begin{cases} \dfrac{\partial \vec{q}_i}{\partial t} = \dfrac{\partial \mathcal{H}}{\partial \vec{p}_i} \\ \dfrac{\partial \vec{p}_i}{\partial t} = -\dfrac{\partial \mathcal{H}}{\partial \vec{q}_i} \end{cases} , \tag{III.1}$$

where the *Hamiltonian* $\mathcal{H}(\mathbf{p}, \mathbf{q})$, describes the total energy in terms of the set of coordinates $\mathbf{q} \equiv \{\vec{q}_1, \vec{q}_2, \cdots, \vec{q}_N\}$, and momenta $\mathbf{p} \equiv \{\vec{p}_1, \vec{p}_2, \cdots, \vec{p}_N\}$. The microscopic equations of motion have *time reversal symmetry*, i.e. if all the momenta are suddenly reversed, $\mathbf{p} \to -\mathbf{p}$, at $t = 0$, the particles retrace their previous trajectory, $\mathbf{q}(t) = \mathbf{q}(-t)$. This follows from the invariance of $\mathcal{H}$ under the transformation $T(\mathbf{p}, \mathbf{q}) \to (-\mathbf{p}, \mathbf{q})$.

As formulated within thermodynamics, the *macrostate* M, of an ideal gas in equilibrium is described by a small number of state functions such as E, T, P, and N. The space of macrostates is considerably smaller than the phase space spanned by microstates. Therefore, there must be a very large number of microstates μ corresponding to the same macrostate M.

This many to one correspondence suggests the introduction of a statistical *ensemble* of microstates. Consider $\mathcal{N}$ copies of a particular macrostate, each described by a different *representative point* $\mu_n(t)$, in the phase space Γ. Let $d\mathcal{N}(\mathbf{p},\mathbf{q},t)$ equal the number of representative points in an infinitesimal volume $d\Gamma = \prod_{i=1}^{N} d^3\vec{p}_i d^3\vec{q}_i$ around the point $(\mathbf{p},\mathbf{q})$. A phase space density $\rho(\mathbf{p},\mathbf{q},t)$ is then defined from

$$\rho(\mathbf{p},\mathbf{q},t)d\Gamma = \lim_{\mathcal{N}\to\infty} \frac{d\mathcal{N}(\mathbf{p},\mathbf{q},t)}{\mathcal{N}}. \tag{III.2}$$

This quantity can be compared with the *objective* probability introduced in the previous section. Clearly $\int d\Gamma \rho = 1$, and ρ is a properly normalized *probability density function* in phase space. To compute macroscopic values for various functions $\mathcal{O}(\mathbf{p},\mathbf{q})$, we shall use the *ensemble averages*

$$\langle \mathcal{O} \rangle = \int d\Gamma \rho(\mathbf{p},\mathbf{q},t)\mathcal{O}(\mathbf{p},\mathbf{q}). \tag{III.3}$$

When the exact microstate μ is specified, the system is said to be in a *pure state*. On the other hand, when our knowledge of the system is probabilistic, in the sense of its being taken from an ensemble with density $\rho(\Gamma)$, it is said to belong to a *mixed state*. It is difficult to describe equilibrium in the context of a pure state, since $\mu(t)$ is constantly changing in time according to eqs.(III.1). Equilibrium is more conveniently described for mixed states by examining the time evolution of the phase space density $\rho(t)$, which is governed by the Liouville's equation introduced in the next section.

III.B Liouville's Theorem

• **Liouville's Theorem** *states that the phase space density $\rho(\Gamma,t)$, behaves like an incompressible fluid.*

Proof: Follow the evolution of $d\mathcal{N}$ pure states in an infinitesimal volume $d\Gamma = \prod_{i=1}^{N} d^3\vec{p}_i d^3\vec{q}_i$ around the point $(\mathbf{p},\mathbf{q})$. According to eqs.(III.1), after an interval δt these states have moved to the vicinity of another point $(\mathbf{p}',\mathbf{q}')$, where

$$q'_\alpha = q_\alpha + \dot{q}_\alpha \delta t + \mathcal{O}(\delta t^2) \quad , \quad p'_\alpha = p_\alpha + \dot{p}_\alpha \delta t + \mathcal{O}(\delta t^2). \tag{III.4}$$

In the above expression, the q_α and p_α refer to any of the $6N$ coordinates and momenta, and $\dot{q}_\alpha$ and $\dot{p}_\alpha$ are the corresponding velocities. The original volume element $d\Gamma$, is in the shape of a hyper-cube of sides dp_α and dq_α. In the time interval δt it gets distorted, and the projected sides of the new volume element are given by

$$\begin{cases} dq'_\alpha = dq_\alpha + \dfrac{\partial \dot{q}_\alpha}{\partial q_\alpha} dq_\alpha \delta t + \mathcal{O}(\delta t^2) \\ dp'_\alpha = dp_\alpha + \dfrac{\partial \dot{p}_\alpha}{\partial p_\alpha} dp_\alpha \delta t + \mathcal{O}(\delta t^2) \end{cases} . \tag{III.5}$$

To order of δt^2, the new volume element is $d\Gamma' = \prod_{i=1}^{N} d^3\vec{p}_i\,' d^3\vec{q}_i\,'$. From eqs.(III.5) it follows that for each pair of conjugate coordinates

$$dq'_\alpha \cdot dp'_\alpha = dq_\alpha \cdot dp_\alpha \left[1 + \left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right) \delta t + \mathcal{O}(\delta t^2)\right]. \tag{III.6}$$

But since the time evolution of coordinates and momenta are governed by the canonical eqs.(III.1), we have

$$\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial}{\partial q_\alpha}\frac{\partial \mathcal{H}}{\partial p_\alpha} = \frac{\partial^2 \mathcal{H}}{\partial p_\alpha \partial q_\alpha}, \quad \text{and} \quad \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} = \frac{\partial}{\partial p_\alpha}\left(-\frac{\partial \mathcal{H}}{\partial q_\alpha}\right) = -\frac{\partial^2 \mathcal{H}}{\partial q_\alpha \partial p_\alpha}. \tag{III.7}$$

Thus the projected area in eq.(III.6) is unchanged for any pair of coordinates, and hence the volume element is unaffected, $d\Gamma' = d\Gamma$. All the pure states $d\mathcal{N}$, originally in the vicinity of $(\mathbf{p}, \mathbf{q})$ are transported to the neighborhood of $(\mathbf{p}', \mathbf{q}')$, but occupy exactly the same volume. The ratio $d\mathcal{N}/d\Gamma$ is left unchanged, and ρ behaves like the density of an incompressible fluid.

The incompressibility condition $\rho(\mathbf{p}', \mathbf{q}', t + \delta t) = \rho(\mathbf{p}, \mathbf{q}, t)$, can be written in differential form as

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N}\left(\frac{\partial \rho}{\partial p_\alpha}\cdot\frac{dp_\alpha}{dt} + \frac{\partial \rho}{\partial q_\alpha}\cdot\frac{dq_\alpha}{dt}\right) = 0. \tag{III.8}$$

Note the distinction between $\partial\rho/\partial t$ and $d\rho/dt$: The former *partial* derivative refers to the changes in ρ at a particular location in phase space, while the latter *total* derivative follows the evolution of a volume of fluid as it moves in phase space. Substituting from eq.(III.1) into eq.(III.8) leads to

$$\frac{\partial \rho}{\partial t} = \sum_{\alpha=1}^{3N}\left(\frac{\partial \rho}{\partial p_\alpha}\cdot\frac{\partial \mathcal{H}}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha}\cdot\frac{\partial \mathcal{H}}{\partial p_\alpha}\right) = -\{\rho, \mathcal{H}\}, \tag{III.9}$$

where we have introduced the *Poisson bracket* of two functions in phase space as

$$\{A, B\} \equiv \sum_{\alpha=1}^{3N} \left(\frac{\partial A}{\partial q_\alpha} \cdot \frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha} \cdot \frac{\partial B}{\partial q_\alpha} \right) = -\{B, A\}. \tag{III.10}$$

(1) Under the action of time reversal, $(\mathbf{p}, \mathbf{q}, t) \to (-\mathbf{p}, \mathbf{q}, -t)$, the Poisson bracket $\{\rho, \mathcal{H}\}$ changes sign, and eq.(III.9) implies that the density reverses its evolution, i.e. $\rho(\mathbf{p}, \mathbf{q}, t) = \rho(-\mathbf{p}, \mathbf{q}, -t)$.

(2) The time evolution of the ensemble average in eq.(III.3) is given by (using eq.(III.9))

$$\frac{d\langle \mathcal{O} \rangle}{dt} = \int d\Gamma \frac{\partial \rho(\mathbf{p}, \mathbf{q}, t)}{\partial t} \mathcal{O}(\mathbf{p}, \mathbf{q}) = \sum_{\alpha=1}^{3N} \int d\Gamma \mathcal{O}(\mathbf{p}, \mathbf{q}) \left(\frac{\partial \rho}{\partial p_\alpha} \cdot \frac{\partial \mathcal{H}}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha} \cdot \frac{\partial \mathcal{H}}{\partial p_\alpha} \right). \tag{III.11}$$

The partial derivatives of ρ in the above equation can be removed by using the method of integration by parts, i.e. $\int f\rho' = -\int \rho f'$ since ρ vanishes on the boundaries of the integrations, leading to

$$\begin{aligned} \frac{d\langle \mathcal{O} \rangle}{dt} &= -\sum_{\alpha=1}^{3N} \int d\Gamma \rho \left[\left(\frac{\partial \mathcal{O}}{\partial p_\alpha} \cdot \frac{\partial \mathcal{H}}{\partial q_\alpha} - \frac{\partial \mathcal{O}}{\partial q_\alpha} \cdot \frac{\partial \mathcal{H}}{\partial p_\alpha} \right) + \mathcal{O} \left(\frac{\partial^2 \mathcal{H}}{\partial p_\alpha \partial q_\alpha} - \frac{\partial^2 \mathcal{H}}{\partial q_\alpha \partial p_\alpha} \right) \right] \\ &= -\int d\Gamma \rho \{\mathcal{H}, \mathcal{O}\} = \langle \{\mathcal{O}, \mathcal{H}\} \rangle . \end{aligned} \tag{III.12}$$

Note that the total time derivative *cannot* be taken inside the integral sign, i.e.

$$\frac{d\langle \mathcal{O} \rangle}{dt} \neq \int d\Gamma \frac{d\rho(\mathbf{p}, \mathbf{q}, t)}{dt} \mathcal{O}(\mathbf{p}, \mathbf{q}). \tag{III.13}$$

This common mistake yields $d\langle \mathcal{O} \rangle / dt = 0$!

(3) If the members of the ensemble correspond to an equilibrium macroscopic state, the ensemble averages must be independent of time. This can be achieved by a stationary density, $\partial \rho_{\rm eq}/\partial t = 0$, i.e. by requiring

$$\{\rho_{\rm eq}, \mathcal{H}\} = 0. \tag{III.14}$$

A possible solution to the above equation is for $\rho_{\rm eq}$ to be a function of $\mathcal{H}$, i.e. $\rho_{\rm eq}(\mathbf{p}, \mathbf{q}) = \rho\big(\mathcal{H}(\mathbf{p}, \mathbf{q})\big)$. It is then easy to verify that $\{\rho(\mathcal{H}), \mathcal{H}\} = \rho'(\mathcal{H})\{\mathcal{H}, \mathcal{H}\} = 0$. This solution implies that the value of ρ is constant on surfaces of constant energy $\mathcal{H}$, in phase space. This is indeed the *basic assumption of statistical mechanics*. For example, in the microcanonical ensemble, the total energy E of an isolated system is specified. All members of the ensemble

must then be located on the surface $\mathcal{H}(\mathbf{p},\mathbf{q}) = E$ in phase space. Eq.(III.9) implies that a uniform density of points on this surface is stationary in time. The assumption of statistical mechanics is that the macrostate is indeed represented by such a uniform density of microstates. This is equivalent to replacing the objective measure of probability in eq.(III.2) with a subjective one.

There may be additional *conserved quantities* associated with the Hamiltonian which satisfy $\{L_n, \mathcal{H}\} = 0$. In the presence of such quantities, a stationary density exists for any function of the form $\rho_{\rm eq}(\mathbf{p},\mathbf{q}) = \rho\big(\mathcal{H}(\mathbf{p},\mathbf{q}), L_1(\mathbf{p},\mathbf{q}), L_2(\mathbf{p},\mathbf{q}), \cdots\big)$. Clearly, the value of L_n is not changed during the evolution of the system, since

$$\begin{aligned}\frac{dL_n(\mathbf{p},\mathbf{q})}{dt} \equiv& \frac{L_n\left(\mathbf{p}(t+dt),\mathbf{q}(t+dt)\right) - L_n\left(\mathbf{p}(t),\mathbf{q}(t)\right)}{dt} \\ =& \sum_{\alpha=1}^{3N}\left(\frac{\partial L_n}{\partial p_\alpha}\cdot\frac{\partial p_\alpha}{\partial t} + \frac{\partial L_n}{\partial q_\alpha}\cdot\frac{\partial q_\alpha}{\partial t}\right) \\ =& -\sum_{\alpha=1}^{3N}\left(\frac{\partial L_n}{\partial p_\alpha}\cdot\frac{\partial \mathcal{H}}{\partial q_\alpha} - \frac{\partial L_n}{\partial q_\alpha}\cdot\frac{\partial \mathcal{H}}{\partial p_\alpha}\right) = \{L_n,\mathcal{H}\} = 0.\end{aligned} \tag{III.15}$$

Hence, the functional dependence of $\rho_{\rm eq}$ on these quantities merely indicates that all *accessible states*, i.e. those that can be connected without violating any conservation law, are equally likely.

(4) The above postulate for $\rho_{\rm eq}$ answers the first question posed at the beginning of this chapter. However, in order to answer the second question, and to justify the basic assumption of statistical mechanics, we need to show that non-stationary densities converge onto the stationary solution $\rho_{\rm eq}$. This contradicts the time reversal symmetry noted in **(1)** above: For any solution $\rho(t)$ converging to $\rho_{\rm eq}$, there is a time reversed solution that diverges from it. The best that can be hoped for is to show that the solutions $\rho(t)$ are in the neighborhood of $\rho_{\rm eq}$ the majority of the time, so that *time averages* are dominated by the stationary solution. This brings us to the problem of *ergodicity*, which is whether it is justified to replace time averages with ensemble averages. In measuring the properties of any system, we deal with only one representative of the equilibrium ensemble. However, most macroscopic properties do not have instantaneous values and require some form of averaging. For example, the pressure P exerted by a gas results from the impact of particles on the walls of the container. The number and momenta of these particles varies at different times and different locations. The measured pressure reflects an average over many characteristic microscopic times. If over this time scale the representative point of

the system moves around and uniformly samples the accessible points in phase space, we may replace the time average with the ensemble average. For a few systems it is possible to prove an *ergodic theorem*, which states that the representative point comes arbitrarily close to all accessible points in phase space after a sufficiently long time. However, the proof usually works for time intervals that grow exponentially with the number of particles N, and thus exceed by far any reasonable time scale over which the pressure of a gas is typically measured. As such the proofs of the ergodic theorem have so far little to do with the reality of macroscopic equilibrium.

III.C The Bogoliubov-Born-Green-Kirkwood-Yvon Hierarchy

The full phase space density contains much more information than necessary for description of equilibrium properties. For example, knowledge of the one particle distribution is sufficient for computing the pressure of a gas. A one particle density refers to the expectation value of finding *any* of the N particles at location $\vec{q}$, with momentum $\vec{p}$, at time t, which is computed from the full density ρ as

$$\begin{aligned} f_1(\vec{p},\vec{q},t) =& \left\langle \sum_{i=1}^{N} \delta^3(\vec{p}-\vec{p}_i)\delta^3(\vec{q}-\vec{q}_i) \right\rangle \\ =& N \int \prod_{i=2}^{N} d^3\vec{p}_i d^3\vec{q}_i \rho(\vec{p}_1=\vec{p},\vec{q}_1=\vec{q},\vec{p}_2,\vec{q}_2,\cdots,\vec{p}_N,\vec{q}_N,t). \end{aligned} \tag{III.16}$$

To obtain the second identity above, we used the first pair of delta functions to perform one set of integrals, and then assumed that the density is symmetric with respect to permuting the particles. Similarly, a two particle density can be computed from

$$f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,t) = N(N-1)\int \prod_{i=3}^{N} dV_i \ \rho(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,\cdots,\vec{p}_N,\vec{q}_N,t), \tag{III.17}$$

where $dV_i = d^3\vec{p}_i d^3\vec{q}_i$ is the contribution of particle i to phase space volume. The general s-particle density is defined by

$$f_s(\vec{p}_1,\cdots,\vec{q}_s,t) = \frac{N!}{(N-s)!}\int \prod_{i=s+1}^{N} dV_i \ \rho(\mathbf{p},\mathbf{q},t) = \frac{N!}{(N-s)!}\rho_s(\vec{p}_1,\cdots,\vec{q}_s,t), \tag{III.18}$$

where ρ_s is a standard *unconditional PDF* for the coordinates of s particles, and $\rho_N \equiv \rho$. While ρ_s is properly normalized to unity when integrated over all its variables, the s-particle density has a normalization of $N!/(N-s)!$. We shall use the two quantities interchangeably.

The evolution of the few-body densities is governed by the BBGKY hierarchy of equations attributed to Bogoliubov, Born, Green, Kirkwood, and Yvon. The simplest non-trivial Hamiltonian studied in kinetic theory is

$$\mathcal{H}(\mathbf{p},\mathbf{q}) = \sum_{i=1}^{N}\left[\frac{\vec{p}_i{}^2}{2m} + U(\vec{q}_i)\right] + \frac{1}{2}\sum_{(i,j)=1}^{N} \mathcal{V}(\vec{q}_i-\vec{q}_j). \tag{III.19}$$

This Hamiltonian provides an adequate description of a weakly interacting gas. In addition to the classical kinetic energy of particles of mass m, it contains an *external potential*

U, and a *two-body interaction* $\mathcal{V}$, between the particles. In principle, three and higher body interactions should also be included for a realistic description, but they are not very important in the dilute gas (nearly ideal) limit.

For evaluating the time evolution of f_s, it is convenient to divide the Hamiltonian into

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_{N-s} + \mathcal{H}', \tag{III.20}$$

where $\mathcal{H}_s$ and $\mathcal{H}_{N-s}$ include only interactions among each group of particles,

$$\begin{aligned} \mathcal{H}_s &= \sum_{n=1}^{s} \left[\frac{\vec{p}_n{}^2}{2m} + U(\vec{q}_n) \right] + \frac{1}{2} \sum_{(n,m)=1}^{s} \mathcal{V}(\vec{q}_n - \vec{q}_m), \\ \mathcal{H}_{N-s} &= \sum_{i=s+1}^{N} \left[\frac{\vec{p}_i{}^2}{2m} + U(\vec{q}_i) \right] + \frac{1}{2} \sum_{(i,j)=s+1}^{N} \mathcal{V}(\vec{q}_i - \vec{q}_j), \end{aligned} \tag{III.21}$$

while the interparticle interactions are contained in

$$\mathcal{H}' = \sum_{n=1}^{s} \sum_{i=s+1}^{N} \mathcal{V}(\vec{q}_n - \vec{q}_i). \tag{III.22}$$

From eq.(III.18), the time evolution of f_s (or ρ_s) is obtained as

$$\frac{\partial \rho_s}{\partial t} = \int \prod_{i=s+1}^{N} dV_i \; \frac{\partial \rho}{\partial t} = -\int \prod_{i=s+1}^{N} dV_i \; \{\rho, \mathcal{H}_s + \mathcal{H}_{N-s} + \mathcal{H}'\}, \tag{III.23}$$

where eq.(III.9) is used for the evolution of ρ. The three Poisson brackets in eq.(III.23) will now be evaluated in turn. Since the first s coordinates are not integrated, the order of integrations and differentiations for the Poisson bracket may be reversed, and

$$\int \prod_{i=s+1}^{N} dV_i \; \{\rho, \mathcal{H}_s\} = \{ \left(\int \prod_{i=s+1}^{N} dV_i \; \rho \right), \mathcal{H}_s \} = \{\rho_s, \mathcal{H}_s\}. \tag{III.24}$$

Writing the Poisson brackets explicitly, the second term of eq.(III.23) takes the form

$$-\int \prod_{i=s+1}^{N} dV_i \; \{\rho, \mathcal{H}_{N-s}\} = \int \prod_{i=s+1}^{N} dV_i \; \sum_{j=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \cdot \frac{\partial \mathcal{H}_{N-s}}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j} \cdot \frac{\partial \mathcal{H}_{N-s}}{\partial \vec{p}_j} \right]$$

(using eq.(III.21))

$$= \int \prod_{i=s+1}^{N} dV_i \; \sum_{j=s+1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \cdot \left(\frac{\partial U}{\partial \vec{q}_j} + \frac{1}{2} \sum_{k=s+1}^{N} \frac{\partial \mathcal{V}(\vec{q}_j - \vec{q}_k)}{\partial \vec{q}_j} \right) - \frac{\partial \rho}{\partial \vec{q}_j} \cdot \frac{\vec{p}_j}{m} \right] = 0. \tag{III.25}$$

The last equality is obtained after performing the integrations by part: The term multiplying $\partial\rho/\partial\vec{p}_j$ has no dependence on $\vec{p}_j$, while $\vec{p}_j/m$ does not depend on $\vec{q}_j$. The final term in eq.(III.23), involving the Poisson bracket with $\mathcal{H}'$, is

$$\begin{aligned}
&\int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N} \left[\frac{\partial\rho}{\partial\vec{p}_j} \cdot \frac{\partial\mathcal{H}'}{\partial\vec{q}_j} - \frac{\partial\rho}{\partial\vec{q}_j} \cdot \frac{\partial\mathcal{H}'}{\partial\vec{p}_j} \right] \\
&= \int \prod_{i=s+1}^{N} dV_i \left[\sum_{n=1}^{s} \frac{\partial\rho}{\partial\vec{p}_n} \cdot \sum_{j=s+1}^{N} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_j)}{\partial\vec{q}_n} + \sum_{j=s+1}^{N} \frac{\partial\rho}{\partial\vec{p}_j} \cdot \sum_{n=1}^{s} \frac{\partial\mathcal{V}(\vec{q}_j - \vec{q}_n)}{\partial\vec{q}_j} \right],
\end{aligned}$$

where the sum over all particles has been subdivided into the two groups. (Note that $\mathcal{H}'$ in eq.(III.22) has no dependence on the momenta.) Integration by parts shows that the second term in the above expression is zero. The first term involves the sum of $(N-s)$ expressions that are equal by symmetry and simplifies to

$$\begin{aligned}
&(N-s) \int \prod_{i=s+1}^{N} dV_i \sum_{n=1}^{s} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial\vec{q}_n} \cdot \frac{\partial\rho}{\partial\vec{p}_n} \\
=&(N-s) \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial\vec{q}_n} \cdot \frac{\partial}{\partial\vec{p}_n} \left[\int \prod_{i=s+2}^{N} dV_i \; \rho \right].
\end{aligned} \tag{III.26}$$

Note that the quantity in the above square brackets is ρ_{s+1}. Thus, adding up eqs.(III.24), (III.25), and (III.26),

$$\frac{\partial\rho_s}{\partial t} - \{\mathcal{H}_s, \rho_s\} = (N-s) \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial\vec{q}_n} \cdot \frac{\partial\rho_{s+1}}{\partial\vec{p}_n} \quad , \tag{III.27}$$

or in terms of the densities f_s,

$$\frac{\partial f_s}{\partial t} - \{\mathcal{H}_s, f_s\} = \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial\mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial\vec{q}_n} \cdot \frac{\partial f_{s+1}}{\partial\vec{p}_n} \quad . \tag{III.28}$$

In the absence of interactions with other particles, the density ρ_s for a group of s particles evolves as the density of an incompressible fluid (as required by Liouville's theorem), and is described by the *streaming terms* on the left hand side of eq.(III.27). However, because of interactions with the remaining $N-s$ particles, the flow is modified by the *collision terms* on the right hand side. The collision integral is the sum of the terms corresponding to a potential collision of any of the particles in the group of s, with any of the remaining $N-s$ particles. To describe the probability of finding the additional particle that collides with a member of this group, the result must depend on the joint PDF of $s+1$ particles described by ρ_{s+1}. This results in a hierarchy of equations in which $\partial\rho_1/\partial t$ depends on ρ_2, $\partial\rho_2/\partial t$ depends on ρ_3, etc., which is at least as complicated as the original equation for the full phase space density. To proceed further, a physically motivated approximation for terminating the hierarchy is needed.

III.D The Boltzmann Equation

To estimate the relative importance of the different terms appearing in eqs.(III.28), let us examine the first two equations in the hierarchy,

$$\left[\frac{\partial}{\partial t}-\frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1}+\frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial \vec{q}_1}\right]f_1=\int dV_2\;\frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\frac{\partial f_2}{\partial \vec{p}_1}, \tag{III.29}$$

and

$$\left[\frac{\partial}{\partial t}-\frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1}-\frac{\partial U}{\partial \vec{q}_2}\cdot\frac{\partial}{\partial \vec{p}_2}+\frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial \vec{q}_1}+\frac{\vec{p}_2}{m}\cdot\frac{\partial}{\partial \vec{q}_2}-\frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\left(\frac{\partial}{\partial \vec{p}_1}-\frac{\partial}{\partial \vec{p}_2}\right)\right]f_2=$$
$$\int dV_3\;\left[\frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_3)}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1}+\frac{\partial \mathcal{V}(\vec{q}_2-\vec{q}_3)}{\partial \vec{q}_2}\cdot\frac{\partial}{\partial \vec{p}_2}\right]f_3\quad . \tag{III.30}$$

Note that two of the streaming terms in eq.(III.30) have been combined by using $\partial\mathcal{V}(\vec{q}_1-\vec{q}_2)/\partial\vec{q}_1 = -\partial\mathcal{V}(\vec{q}_2-\vec{q}_1)/\partial\vec{q}_2$, which is valid for a *symmetric* potential such that $\mathcal{V}(\vec{q}_1-\vec{q}_2)=\mathcal{V}(\vec{q}_2-\vec{q}_1)$.

• *Time scales:* All terms within square brackets in the above equations have dimensions of inverse time, and we estimate their relative magnitudes by dimensional analysis, using typical velocities and length scales. The typical speed of a gas particle at room temperature is $v\approx 10^2 ms^{-1}$. For terms involving the external potential U, or the inter-atomic potential $\mathcal{V}$, an appropriate length scale can be extracted from the range of variations of the potential.

(a) The terms proportional to

$$\frac{1}{\tau_U}\sim\frac{\partial U}{\partial \vec{q}}\cdot\frac{\partial}{\partial \vec{p}}\;,$$

involve spatial variations of the external potential $U(\vec{q})$, which take place over macroscopic distances L. We shall refer to the associated time τ_U, as an *extrinsic* time scale, as it can be made arbitrarily long by increasing system size. For a typical value of $L\approx 10^{-3}m$, we get $\tau_U\approx L/v\approx 10^{-5}s$.

(b) From the terms involving the inter-atomic potential $\mathcal{V}$, we can extract two additional time scales, which are *intrinsic* to the gas under study. In particular, the *collision duration*

$$\frac{1}{\tau_c}\sim\frac{\partial \mathcal{V}}{\partial \vec{q}}\cdot\frac{\partial}{\partial \vec{p}}\;,$$

is the typical time over which two particles are within the effective range d, of their interaction. For *short range* interactions (including van der Waals and Lenard–Jones, despite their power law decaying tails), $d\approx 10^{-10}m$ is of the order of a typical atomic size, resulting in $\tau_c\approx 10^{-12}s$. This is usually the shortest time scale in the problem.

The analysis is somewhat more complicated for *long range* interactions, such as the Coulomb gas in a plasma. For a neutral plasma, the Debye screening length λ replaces d in the above equation, as discussed in the problems.

(c) There are also collision terms on the right hand side of eqs.(III.28), which depend on f_{s+1}, and lead to an inverse time scale

$$\frac{1}{\tau_\times} \sim \int dV \; \frac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \; \frac{f_{s+1}}{f_s} \sim \int dV \; \frac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \; N \frac{\rho_{s+1}}{\rho_s}.$$

The integrals are only non-zero over the volume of the inter-particle potential d^3. The term f_{s+1}/f_s is related to the probability of finding another particle per unit volume, which is roughly the particle density $n = N/V \approx 10^{26} m^{-3}$. We thus obtain the *mean free time*

$$\tau_\times \approx \frac{\tau_c}{nd^3} \approx \frac{1}{nvd^2}, \tag{III.31}$$

which is the typical distance a particle travels between collisions. For short range interactions, $\tau_\times \approx 10^{-8} s$ is much longer than τ_c, and the collision terms on the right hand side of eqs.(III.28) are smaller by a factor of $nd^3 \approx (10^{26} m^{-3})(10^{-10} m)^3 \approx 10^{-4}$.

The *Boltzmann equation* is obtained for short range interactions in the dilute regime by exploiting $\tau_c/\tau_\times \approx nd^3 \ll 1$. (By contrast, for long range interactions such that $nd^3 \gg 1$, the *Vlasov equation* is obtained by dropping the collision terms on the left hand side, as discussed in the problems.) From the above discussion, it is apparent that eq.(III.29) is different from the rest of the hierarchy: It is the only one in which the collision terms are absent from the left hand side. For all other equations, the right hand side is smaller by a factor of nd^3, while in eq.(III.29) it may indeed dominate the left hand side. Thus a possible approximation scheme is to truncate the equations after the first two, by setting the right hand side of eq.(III.30) to zero.

Setting the right hand side of the equation for f_2 to zero implies that the two body density evolves as in an isolated two-particle system. The relatively simple mechanical processes that govern this evolution result in streaming terms for f_2 which are proportional to both τ_U^{-1} and τ_c^{-1}. The two sets of terms can be more or less treated independently: the former describe the evolution of the center of mass of the two particles, while the latter govern the dependence on relative coordinates.

The density f_2 is proportional to the joint PDF ρ_2 for finding one particle at $(\vec{p}_1, \vec{q}_1)$, and another at $(\vec{p}_2, \vec{q}_2)$, at the same time t. It is reasonable to expect that at distances much larger than the range of the potential $\mathcal{V}$, the particles are independent, i.e.

$$\begin{cases} \rho_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, t) \longrightarrow \rho_1(\vec{p}_1, \vec{q}_1, t)\rho_1(\vec{p}_2, \vec{q}_2, t), & \text{or} \\ f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, t) \longrightarrow f_1(\vec{p}_1, \vec{q}_1, t)f_1(\vec{p}_2, \vec{q}_2, t), & \text{for} \quad |\vec{q}_2 - \vec{q}_1| \gg d. \end{cases} \tag{III.32}$$

The above statement should be true even for situations out of equilibrium. For example, imagine that the gas particles in a chamber are suddenly allowed to invade an empty volume after the removal of a barrier. The density f_1 will undergo a complicated evolution, and its relaxation time will be at least comparable to τ_U. The two particle density f_2, will also reach its final value at a comparable time interval. However, it is expected to relax to a form similar to eq.(III.32) over a much shorter time of the order of τ_c.

For the collision term on the right hand side of eq.(III.29), we actually need the precise dependence of f_2 on the relative coordinates and momenta at separations comparable to d. At time intervals longer than τ_c (but possibly shorter than τ_U), the 'steady state' behavior of f_2 at small relative distances is obtained by equating the largest streaming terms in eq.(III.30), i.e.

$$\left[\frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial\vec{q}_1} + \frac{\vec{p}_2}{m}\cdot\frac{\partial}{\partial\vec{q}_2} - \frac{\partial\mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial\vec{q}_1}\cdot\left(\frac{\partial}{\partial\vec{p}_1} - \frac{\partial}{\partial\vec{p}_2}\right)\right] f_2 = 0. \tag{III.33}$$

We expect $f_2(\vec{q}_1, \vec{q}_2)$ to have slow variations over the center of mass coordinate $\vec{Q} = (\vec{q}_1 + \vec{q}_2)/2$, and large variations over the relative coordinate $\vec{q} = \vec{q}_2 - \vec{q}_1$. Therefore, $\partial f_2/\partial\vec{q} \gg \partial f_2/\partial\vec{Q}$, and $\partial f_2/\vec{q}_2 \approx -\partial f_2/\partial\vec{q}_1 \approx \partial f_2/\partial\vec{q}$, leading to

$$\frac{\partial\mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial\vec{q}_1}\cdot\left(\frac{\partial}{\partial\vec{p}_1} - \frac{\partial}{\partial\vec{p}_2}\right) f_2 = -\left(\frac{\vec{p}_1-\vec{p}_2}{m}\right)\cdot\frac{\partial}{\partial\vec{q}} f_2 \quad . \tag{III.34}$$

The above equation provides a precise mathematical expression for how f_2 is constrained along the trajectories that describe the collision of the two particles.

The collision term on the right hand side of eq.(III.29) can now be written as

$$\begin{aligned} \left.\frac{df_1}{dt}\right|_{\text{coll.}} &= \int d^3\vec{p}_2 d^3\vec{q}_2 \; \frac{\partial\mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial\vec{q}_1}\cdot\left(\frac{\partial}{\partial\vec{p}_1} - \frac{\partial}{\partial\vec{p}_2}\right) f_2 \\ &\approx \int d^3\vec{p}_2 d^3\vec{q} \; \left(\frac{\vec{p}_2-\vec{p}_1}{m}\right)\cdot\frac{\partial}{\partial\vec{q}} f_2\left(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}; t\right) \quad . \end{aligned} \tag{III.35}$$

The first identity if obtained from eq.(III.29) by noting that the added term proportional to $\partial f_2/\partial \vec{p}_2$ is a complete derivative and integrates to zero, while the second equality follows from eq.(III.34), after the change of variables to $\vec{q} = \vec{q}_2 - \vec{q}_1$. (Since it relies on establishing the 'steady state' in the relative coordinates, this approximation is valid as long as we examine events in time with a resolution longer than τ_c.)

• *Kinematics of collision and scattering:* The integrand in eq.(III.35) is a derivative of f_2 with respect to $\vec{q}$ along the direction of relative motion $\vec{p} = \vec{p}_2 - \vec{p}_1$, of the colliding particles. To perform this integration we introduce a convenient coordinate system for $\vec{q}$, guided by the formalism used to describe the scattering of particles. Naturally, we choose one axis to be parallel to $\vec{p}_2 - \vec{p}_1$, with the corresponding coordinate a which is negative before a collision, and positive afterwards. The other two coordinates of $\vec{q}$ are represented by an *impact vector* $\vec{b}$ which is $\vec{0}$ for a head–on collision ($[\vec{p}_1 - \vec{p}_2] \parallel [\vec{q}_1 - \vec{q}_2]$). We can now integrate over a to get

$$\left.\frac{df_1}{dt}\right|_{\rm coll.} = \int d^3\vec{p}_2\, d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2| \left[f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, +; t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) \right], \qquad \text{(III.36)}$$

where $|\vec{v}_1 - \vec{v}_2| = |\vec{p}_1 - \vec{p}_2|/m$ is the relative speed of the two particles, with $(\vec{b}, -)$ and $(\vec{b}, +)$ referring to relative coordinates before and after the collision. Note that $d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|$ is just the flux of particles impinging on the element of area $d^2\vec{b}$.

In principle, the integration over a is from $-\infty$ to $+\infty$, but as the variations of f_2 are only significant over the interaction range d, we can evaluate the above quantities at separations of a few d from the collision point. This is a good compromise, allowing us to evaluate f_2 away from the collisions, but at small enough separations so that we can ignore the difference between $\vec{q}_1$ and $\vec{q}_2$. This amounts to a coarse-graining in space which eliminates variations on scales finer than d. With these provisos, it is tempting to close the equation for f_1, by using the assumption of uncorrelated particles in eq.(III.32). Clearly some care is necessary as a naive substitution gives zero! The key observation is that the densities f_2 for situations corresponding to before and after the collision have to be treated differently. For example, soon after opening of the slot separating empty and full gas containers, the momenta of the gas particles are likely to point away from the slot. Collisions will tend to randomize momenta, yielding a more isotropic distribution. However, the densities f_2 before and after the collision are related by streaming, implying that $f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, +; t) = f_2(\vec{p}_1\,', \vec{q}_1, \vec{p}_2\,', \vec{b}, -; t)$, where $\vec{p}_1\,'$ and $\vec{p}_2\,'$ are momenta whose collision at an impact vector $\vec{b}$ results in production of outgoing particles with momenta $\vec{p}_1$

and $\vec{p}_2$. They can be obtained using time reversal symmetry, by integrating the equations of motion for incoming colliding particles of momenta $-\vec{p}_1$ and $-\vec{p}_2$. In terms of these momenta, we can write

$$\left.\frac{df_1}{dt}\right|_{\rm coll.} = \int d^3\vec{p}_2\, d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2| \left[f_2(\vec{p}_1\,', \vec{q}_1, \vec{p}_2\,', \vec{b}, -; t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) \right]. \quad \text{(III.37)}$$

It is sometimes more convenient to describe the scattering of two particles in terms of the relative momenta $\vec{p} = \vec{p}_1 - \vec{p}_2$ and $\vec{p}\,' = \vec{p}_1\,' - \vec{p}_2\,'$, before and after the collision. For a given $\vec{b}$, the initial momentum $\vec{p}$ is deterministically transformed to the final momentum $\vec{p}\,'$. To find the functional form $\vec{p}\,'(|\vec{p}|, \vec{b})$, one must integrate the equations of motion. However, it is possible to make some general statements based on conservation laws: In elastic collisions, the magnitude of $\vec{p}$ is preserved, and it merely rotates to a final direction indicated by the angles $(\theta, \phi) \equiv \hat{\Omega}(\vec{b})$ (a unit vector) in spherical coordinates. Since there is a one to one correspondence between the impact vector $\vec{b}$, and the *solid angle* Ω, we make a change of variables between the two, resulting in

$$\left.\frac{df_1}{dt}\right|_{\rm coll.} = \int d^3\vec{p}_2 d^2\Omega \, \left|\frac{d\sigma}{d\Omega}\right| |\vec{v}_1 - \vec{v}_2| \left[f_2(\vec{p}_1\,', \vec{q}_1, \vec{p}_2\,', \vec{b}, -; t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) \right]. \quad \text{(III.38)}$$

The Jacobian of this transformation, $|d\sigma/d\Omega|$, has dimensions of area, and is known as the *differential cross-section*. It is equal to the area presented to an incoming beam which scatters into the solid angle Ω. The out-going momenta $\vec{p}_1\,'$ and $\vec{p}_2\,'$ in eq.(III.38) are now obtained from the two conditions $\vec{p}_1\,' + \vec{p}_2\,' = \vec{p}_1 + \vec{p}_2$ (conservation of momentum), and $\vec{p}_1\,' - \vec{p}_2\,' = |\vec{p}_1 - \vec{p}_2|\hat{\Omega}(\vec{b})$ (conservation of energy), as

$$\begin{cases} \vec{p}_1\,' = \left(\vec{p}_1 + \vec{p}_2 + |\vec{p}_1 - \vec{p}_2|\hat{\Omega}(\vec{b})\right)/2, \\ \vec{p}_2\,' = \left(\vec{p}_1 + \vec{p}_2 - |\vec{p}_1 - \vec{p}_2|\hat{\Omega}(\vec{b})\right)/2. \end{cases} \quad \text{(III.39)}$$

For the scattering of two *hard spheres* of diameter D, it is easy to show that the scattering angle is related to the impact parameter b by $\cos(\theta/2) = b/D$ for all ϕ. The differential cross-section is then obtained from

$$d^2\sigma = b\, db\, d\phi = D\cos\left(\frac{\theta}{2}\right) D\sin\left(\frac{\theta}{2}\right)\frac{d\theta}{2}\, d\phi = \frac{D^2}{4}\sin\theta d\theta\, d\phi = \frac{D^2}{4}\, d^2\Omega.$$

(Note that the solid angle in three dimensions is given by $d^2\Omega = \sin\theta d\theta\, d\phi$.) Integrating over all angles leads to the total cross–section of $\sigma = \pi D^2$, which is evidently correct. The

differential cross-section for hard spheres is *independent* of both θ and $|\vec{P}|$. This is not the case for soft potentials. For example, the Coulomb potential $\mathcal{V} = e^2/|\vec{Q}|$ leads to

$$\left|\frac{d\sigma}{d\Omega}\right| = \left(\frac{me^2}{2|\vec{P}|^2 \sin^2(\theta/2)}\right)^2 .$$

(The dependence on $|\vec{P}|$ can be justified by obtaining a distance of closest approach from $|\vec{P}|^2/m + e^2/b \approx 0$.)

- The Boltzmann equation is obtained from eq.(III.38) after the substitution

$$f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) = f_1(\vec{p}_1, \vec{q}_1, t) \cdot f_1(\vec{p}_2, \vec{q}_1, t), \tag{III.40}$$

known as the *assumption of molecular chaos*. Note that even if one starts with an uncorrelated initial probability distribution for particles, there is no guarantee that correlations are not generated as a result of collisions. The final result is the following closed form equation for f_1

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{q}_1}\right] f_1 = \\ - \int d^3\vec{p}_2 d^2\Omega \left|\frac{d\sigma}{d\Omega}\right| |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1, \vec{q}_1, t) f_1(\vec{p}_2, \vec{q}_1, t) - f_1(\vec{p}_1\,', \vec{q}_1, t) f_1(\vec{p}_2\,', \vec{q}_1, t)\right] . \tag{III.41}$$

Given the complexity of the above 'derivation' of the Boltzmann equation, it is appropriate to provide a heuristic explanation. The streaming terms on the left hand side of the equation describe the motion of a single particle in the external potential U. The collision terms on the right hand side have a simple physical interpretation: The probability of finding a particle of momentum $\vec{p}_1$ at $\vec{q}_1$ is suddenly altered if it undergoes a collision with another particle of momentum $\vec{p}_2$. The probability of such a collision is the product of kinematic factors described by the differential cross-section $|d\sigma/d\Omega|$, the 'flux' of incident particles proportional to $|\vec{v}_2 - \vec{v}_1|$, and the joint probability of finding the two particles, approximated by $f_1(\vec{p}_1) f_1(\vec{p}_2)$. The first term on the right hand side of eq.(III.41) subtracts this probability and integrates over all possible momenta and solid angles describing the collision. The second term represents an *addition* to the probability which results from the inverse process: A particle can suddenly appear with coordinates $(\vec{p}_1, \vec{q}_1)$ as a result of a collision between two particles initially with momenta $\vec{p}_1\,'$ and $\vec{p}_2\,'$. The cross-section, and the momenta $(\vec{p}_1\,', \vec{p}_2\,')$ may have a complicated dependence on $(\vec{p}_1, \vec{p}_2)$ and Ω, determined by the specific form of the potential $\mathcal{V}$. Remarkably, various equilibrium properties of the gas are quite independent of this potential.

III.E The H–Theorem and Irreversibility

The second question posed at the beginning of this chapter was whether a collection of particles naturally evolves towards an equilibrium state. While it is possible to obtain steady state solutions for the full phase space density ρ_N, because of time reversal symmetry these solutions are not attractors of generic non-equilibrium densities. Does the unconditional one particle PDF ρ_1, suffer the same problem? While the exact density ρ_1 must necessarily reflect this property of ρ_N, the H–theorem proves that an approximate ρ_1, governed by the Boltzmann equation, does in fact non-reversibly approach an equilibrium form. This theorem states that:

- *If $f_1(\vec{p},\vec{q},t)$ satisfies the Boltzmann equation, then $d\mathrm{H}/dt \leq 0$, where*

$$\mathrm{H}(t) = \int d^3\vec{p}\, d^3\vec{q}\; f_1(\vec{p},\vec{q},t) \ln f_1(\vec{p},\vec{q},t) \quad . \tag{III.42}$$

The function $\mathrm{H}(t)$ is related to the information content of the one particle PDF. Up to an overall constant, the information content of $\rho_1 = f_1/N$ is given by $I[\rho_1] = \langle \ln \rho_1 \rangle$, which is clearly similar to $\mathrm{H}(t)$.

Proof: The time derivative of H is

$$\frac{d\mathrm{H}}{dt} = \int d^3\vec{p}_1 d^3\vec{q}_1 \;\; \frac{\partial f_1}{\partial t} \left(\ln f_1 + 1\right) = \int d^3\vec{p}_1 d^3\vec{q}_1 \;\; \ln f_1 \frac{\partial f_1}{\partial t} \quad , \tag{III.43}$$

since $\int dV_1 f_1 = N \int d\Gamma \rho = N$ is time independent. Using eq.(III.41), we obtain

$$\frac{d\mathrm{H}}{dt} = \int d^3\vec{p}_1 d^3\vec{q}_1 \;\; \ln f_1 \left(\frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial f_1}{\partial \vec{p}_1} - \frac{\vec{p}_1}{m} \cdot \frac{\partial f_1}{\partial \vec{q}_1} \right)$$
$$- \int d^3\vec{p}_1 d^3\vec{q}_1 d^3\vec{p}_2 d^2\sigma |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1,\vec{q}_1) f_1(\vec{p}_2,\vec{q}_1) - f_1(\vec{p}_1\,',\vec{q}_1) f_1(\vec{p}_2\,',\vec{q}_1) \right] \ln f_1(\vec{p}_1,\vec{q}_1), \tag{III.44}$$

where we shall interchangeably use $d^2\sigma$, $d^2\vec{b}$, or $d^2\Omega|d\sigma/d\Omega|$ for the differential cross-section. The streaming terms in the above expression are zero, as shown through successive integrations by part,

$$\int d^3\vec{p}_1 d^3\vec{q}_1 \;\; \ln f_1 \;\frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial f_1}{\partial \vec{p}_1} = -\int d^3\vec{p}_1 d^3\vec{q}_1 f_1 \;\frac{\partial U}{\partial \vec{q}_1} \cdot \frac{1}{f_1}\frac{\partial f_1}{\partial \vec{p}_1} = \int d^3\vec{p}_1 d^3\vec{q}_1 f_1 \frac{\partial}{\partial \vec{p}_1} \cdot \frac{\partial U}{\partial \vec{q}_1} = 0,$$

and

$$\int d^3\vec{p}_1 d^3\vec{q}_1 \;\; \ln f_1 \;\frac{\vec{p}_1}{m} \cdot \frac{\partial f_1}{\partial \vec{q}_1} = -\int d^3\vec{p}_1 d^3\vec{q}_1 \;\; f_1 \;\frac{\vec{p}_1}{m} \cdot \frac{1}{f_1}\frac{\partial f_1}{\partial \vec{q}_1} = \int d^3\vec{p}_1 d^3\vec{q}_1 f_1 \frac{\partial}{\partial \vec{q}_1} \cdot \frac{\vec{p}_1}{m} = 0.$$

The collision term in eq.(III.44) involves integrations over dummy variables $\vec{p}_1$ and $\vec{p}_2$. The labels (1) and (2) can thus be exchanged without any change in the value of the integral. Averaging the resulting two expressions gives

$$\frac{d\mathrm{H}}{dt} = -\frac{1}{2}\int d^3\vec{q}d^3\vec{p}_1 d^3\vec{p}_2 d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|\,[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')]\ln\left(f_1(\vec{p}_1)f_1(\vec{p}_2)\right). \tag{III.45}$$

(The arguments, $\vec{q}$ and t, of f_1 are suppressed for ease of notation.) We would now like to change the variables of integrations from the coordinates describing the initiators of the collision, $(\vec{p}_1, \vec{p}_2, \vec{b})$, to those of their products, $(\vec{p}_1\,', \vec{p}_2\,', \vec{b}\,')$. The explicit functional forms describing this transformation are complicated because of the dependence of the solid angle $\hat{\Omega}$ in eq.(III.39) on $\vec{b}$ and $|\vec{p}_2 - \vec{p}_1|$. However, we are assured that the Jacobian of the transformation is unity because of time reversal symmetry; since for every collision there is an inverse one obtained by reversing the momenta of the products. In terms of the new coordinates

$$\frac{d\mathrm{H}}{dt} = -\frac{1}{2}\int d^3\vec{q}d^3\vec{p}_1\,' d^3\vec{p}_2\,' d^2\vec{b}\,'|\vec{v}_1 - \vec{v}_2|\,[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')]\ln\left(f_1(\vec{p}_1)f_1(\vec{p}_2)\right), \tag{III.46}$$

where we should now regard $(\vec{p}_1, \vec{p}_2)$ in the above equation, as functions of the integration variables $(\vec{p}_1\,', \vec{p}_2\,', \vec{b}\,')$ as in eq.(III.39). As noted earlier, $|\vec{v}_1 - \vec{v}_2| = |\vec{v}_1\,' - \vec{v}_2\,'|$ for any elastic collision, and we can use these quantities interchangeably. Finally, we relabel the dummy integration variables such that the primes are removed. Noting that the functional dependence of $(\vec{p}_1, \vec{p}_2, \vec{b}\,)$ on $(\vec{p}_1\,', \vec{p}_2\,', \vec{b}\,')$ is exactly the same as its inverse, we obtain

$$\frac{d\mathrm{H}}{dt} = -\frac{1}{2}\int d^3\vec{q}d^3\vec{p}_1 d^3\vec{p}_2 d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|\,[f_1(\vec{p}_1\,')f_1(\vec{p}_2\,') - f_1(\vec{p}_1)f_1(\vec{p}_2)]\ln\left(f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')\right). \tag{III.47}$$

Averaging eqs.(III.45) and (III.47) results in

$$\frac{d\mathrm{H}}{dt} = -\frac{1}{4}\int d^3\vec{q}d^3\vec{p}_1 d^3\vec{p}_2 d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|\,[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')] \left[\ln\left(f_1(\vec{p}_1)f_1(\vec{p}_2)\right) - \ln\left(f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')\right)\right]. \tag{III.48}$$

The integrand of the above expression is always positive. If $f_1(\vec{p}_1)f_1(\vec{p}_2) > f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')$, both terms in square brackets are positive, while both are negative if $f_1(\vec{p}_1)f_1(\vec{p}_2) < f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')$. In either case, their product is positive. The positivity of the integrand establishes the validity of the H–theorem,

$$\frac{d\mathrm{H}}{dt} \leq 0 \quad . \tag{III.49}$$

• *Irreversibility:* The second law is an *empirical* formulation of the vast number of everyday observations which support the existence of an *arrow of time.* Reconciling the reversibility of laws of physics governing the microscopic domain with the observed irreversibility of macroscopic phenomena is a fundamental problem. Of course, not all microscopic laws of physics are reversible: weak nuclear interactions violate time reversal symmetry, and the collapse of the quantum wave-function in the act of observation is irreversible. The former interactions in fact do not play any significant role in everyday observations that lead to the second law. The irreversible collapse of the wave-function may itself be an artifact of treating macroscopic observers and microscopic observables distinctly.† There are proponents of the view that the reversibility of the currently accepted microscopic equations of motion (classical or quantum) is indicative of their inadequacy. However, the advent of powerful computers has made it possible to simulate the evolution of collections of large numbers of particles, governed by *classical, reversible* equations of motion. Although simulations are currently limited to relatively small numbers of particles (10^6), they do exhibit the irreversible macroscopic behaviors similar to those observed in nature (typically involving 10^{23} particles). For example, particles initially occupying one half of a box proceed to irreversibly, and uniformly, occupy the whole box. (This has nothing to do with limitations of computational accuracy; the same macroscopic irreversibility is observed in exactly reversible integer based simulations, such as with cellular automata.) Thus the origin of the observed irreversibilities should be sought in the classical evolution of large collections of particles.

The Boltzmann equation is the first formula we have encountered that is clearly not time reversible, as indicated by eq.(III.49). We can thus ask the question of how we obtained this result from the Hamiltonian equations of motion. The key to this, of course, resides in the physically motivated approximations used to obtain eq.(III.41). The first steps of the approximation were dropping the three body collision term on the right hand side of eq.(III.30), and the implicit coarse–graining of the resolution in the spatial and temporal scales. Neither of these steps explicitly violates time reversal symmetry, and the collision term in eq.(III.37) retains this property. The next step in getting to eq.(III.41) is to replace the two–body density $f_2(-)$, *evaluated before the collision*, with the product of two one body densities according to eq.(III.32). This treats the two body densities before

† The time dependent Schrödinger equation is fully time reversible. If it is possible to write a complicated wave-function that includes the observing apparatus (possibly the whole universe), it is hard to see how any irreversibility may occur.

and after the collision differently. We could have alternatively expressed eq.(III.37) in terms of the two body densities $f_2(+)$ *evaluated after the collision.* Replacing $f_2(+)$ with the product of two one particle densities would then lead to the opposite conclusion, with $d\mathrm{H}/dt \geq 0$! For a system in equilibrium, it is hard to justify one choice over the other. However, once the system is out of equilibrium, the coordinates after the collision are more quite likely to be correlated, and hence the substitution of eq.(III.32) for $f_2(+)$ does not make sense. Time reversal symmetry implies that there should also be subtle correlations in $f_2(-)$ which are ignored in the so-called *assumption of molecular chaos.*

While the assumption of molecular chaos before (but not after) collisions is the key to the irreversibility of the Boltzmann equation, the resulting loss of information is best justified in terms of the coarse graining of space and time: The Liouville equation and its descendants contain precise information about the evolution of a pure state. This information, however, is inevitably transported to shorter scales. A useful image is that of mixing two immiscible fluids. While the two fluids remain distinct at each point, the transitions in space from one to the next occur at finer resolution on subsequent mixing. At some point, a finite resolution in any measuring apparatus will prevent keeping track of the two components. In the Boltzmann equation the precise information of the pure state is lost at the scale of collisions. The resulting one body density only describes space and time resolutions longer than those of a two-body collision, becoming more and more probabilistic as further information is lost.

III.F Equilibrium Properties

What is the nature of the equilibrium state described by f_1, for a homogeneous gas? **(1)** *The equilibrium distribution:* After the gas has reached equilibrium, the function H should no longer decrease with time. Since the integrand in eq.(III.48) is always positive, a *necessary* condition for $d\mathrm{H}/dt = 0$ is that

$$f_1(\vec{p}_1, \vec{q}_1) f_1(\vec{p}_2, \vec{q}_1) - f_1(\vec{p}_1\,', \vec{q}_1) f_1(\vec{p}_2\,', \vec{q}_1) = 0, \tag{III.50}$$

i.e. *at each point* $\vec{q}$, we must have

$$\ln f_1(\vec{p}_1, \vec{q}) + \ln f_1(\vec{p}_2, \vec{q}) = \ln f_1(\vec{p}_1\,', \vec{q}) + \ln f_1(\vec{p}_2\,', \vec{q}). \tag{III.51}$$

The left hand side of the above equation refers to the momenta before a two-body collision, and the right hand side to the those after the collision. The equality is thus satisfied by

any *additive* quantity that is conserved during the collision. There are 5 such conserved quantities for an elastic collision: the particle number, the three components of the net momentum, and the kinetic energy. Hence, a general solution for f_1 is

$$\ln f_1 = a(\vec{q}) - \vec{\alpha}(\vec{q}) \cdot \vec{p} - \beta(\vec{q}) \left(\frac{\vec{p}^{\,2}}{2m} \right). \tag{III.52}$$

We can easily accomodate the potential energy $U(\vec{q})$ in the above form, and set

$$f_1(\vec{p}, \vec{q}) = \mathcal{N}(\vec{q}) \exp \left[-\vec{\alpha}(\vec{q}) \cdot \vec{p} - \beta(\vec{q}) \left(\frac{p^2}{2m} + U(\vec{q}) \right) \right]. \tag{III.53}$$

We shall refer to the above distribution as describing *local equilibrium*. While this form is preserved *during collisions*, it will evolve in time *away from collisions*, due to the streaming terms, unless $\{\mathcal{H}_1, f_1\} = 0$. The latter condition is satisfied for any function f_1 that depends only on $\mathcal{H}_1$, or any other quantity that is conserved by it. Clearly, the above density satisfies this requirement as long as $\mathcal{N}$, and β are independent of $\vec{q}$, and $\vec{\alpha} = 0$.

According to eq.(III.16), the appropriate normalization for f_1 is

$$\int d^3\vec{p}\, d^3\vec{q}\, f_1(\vec{p}, \vec{q}) = N. \tag{III.54}$$

For particles in a box of volume V, the potential $U(\vec{q})$ is zero inside the box, and infinite on the outside. The normalization factor in eq.(III.53) can be obtained from eq.(III.54) as

$$N = \mathcal{N} V \left[\int_{-\infty}^{\infty} dp_i \exp \left(-\alpha_i p_i - \frac{\beta p_i^2}{2m} \right) \right]^3 = \mathcal{N} V \left(\frac{2\pi m}{\beta} \right)^{3/2} \exp \left(\frac{m\alpha^2}{2\beta} \right). \tag{III.55}$$

Hence, the properly normalized Gaussian distribution for momenta is

$$f_1(\vec{p}, \vec{q}) = n \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp \left[-\frac{\beta(\vec{p} - \vec{p}_0)^2}{2m} \right], \tag{III.56}$$

where $\vec{p}_0 = \langle \vec{p} \rangle = m\vec{\alpha}/\beta$ is the mean value for the momentum of the gas, which is zero for a stationary box, and $n = N/V$ is the particle density. From the Gaussian form of the distribution it can be easily concluded that the variance of each component of the momentum is $\langle p_i^2 \rangle = m/\beta$, and

$$\langle p^2 \rangle = \langle p_x^2 + p_y^2 + p_z^2 \rangle = \frac{3m}{\beta} \quad . \tag{III.57}$$

(2) *Equilibrium between two gases:* Consider two different gases (a) and (b), moving in the same potential U, and subject to a two-body interaction $\mathcal{V}_{ab}\left(\vec{q}^{\,(a)} - \vec{q}^{\,(b)}\right)$. We can define one-particle densities, $f_1^{(a)}$, and, $f_1^{(b)}$, for the two gases respectively. In terms of a generalized collision integral

$$C_{\alpha,\beta} = -\int d^3\vec{p}_2 d^2\Omega \left|\frac{d\sigma_{\alpha,\beta}}{d\Omega}\right| |\vec{v}_1 - \vec{v}_2| \left[f_1^{(\alpha)}(\vec{p}_1,\vec{q}_1) f_1^{(\beta)}(\vec{p}_2,\vec{q}_1) - f_1^{(\alpha)}(\vec{p}_1\,',\vec{q}_1) f_1^{(\beta)}(\vec{p}_2\,',\vec{q}_1)\right], \tag{III.58}$$

the evolution of these densities is governed by a simple generalization of the Boltzmann equation to

$$\begin{cases} \dfrac{\partial f_1^{(a)}}{\partial t} = -\left\{f_1^{(a)}, \mathcal{H}_1^{(a)}\right\} + C_{a,a} + C_{a,b} \\ \dfrac{\partial f_1^{(b)}}{\partial t} = -\left\{f_1^{(b)}, \mathcal{H}_1^{(b)}\right\} + C_{b,a} + C_{b,b} \end{cases} . \tag{III.59}$$

Stationary distributions can be obtained if all six terms on the right hand side of eqs.(III.59) are zero. In the absence of inter-species collisions, i.e. for $C_{a,b} = C_{b,a}$, we can obtain independent stationary distributions $f_1^{(a)} \propto \exp\left(-\beta_a \mathcal{H}_1^{(a)}\right)$ and $f_1^{(b)} \propto \exp\left(-\beta_b \mathcal{H}_1^{(b)}\right)$. Requiring the vanishing of $C_{a,b}$ leads to the additional constraint,

$$\begin{aligned} f_1^{(a)}(\vec{p}_1) f_1^{(b)}(\vec{p}_2) - f_1^{(a)}(\vec{p}_1\,') f_1^{(b)}(\vec{p}_2\,') = 0, \quad \Longrightarrow \\ \beta_a \mathcal{H}_1^{(a)}(\vec{p}_1) + \beta_b \mathcal{H}_1^{(b)}(\vec{p}_2) = \beta_a \mathcal{H}_1^{(a)}(\vec{p}_1\,') + \beta_b \mathcal{H}_1^{(b)}(\vec{p}_2\,') \quad . \end{aligned} \tag{III.60}$$

Since the total energy $\mathcal{H}_1^{(a)} + \mathcal{H}_1^{(b)}$ is conserved in a collision, the above equation can be satisfied for $\beta_a = \beta_b = \beta$. From eq.(III.57) this condition implies the equality of the kinetic energies of the two species,

$$\left\langle \frac{p_a^2}{2m_a} \right\rangle = \left\langle \frac{p_b^2}{2m_b} \right\rangle = \frac{3}{2\beta} \quad . \tag{III.61}$$

The parameter β thus plays the role of an *empirical temperature* describing the equilibrium of gases.

(3) *The equation of state:* To complete the identification of β with temperature T, consider a gas of N particles confined to a box of volume V. The gas pressure results from the force exerted by the particles colliding with the walls of the container. Consider a wall element of area A perpendicular to the x direction. The number of particles impacting this area, with momenta in the interval $[\vec{p}, \vec{p} + d\vec{p}]$, over a time period δt, is

$$d\mathcal{N}(\vec{p}) = \left(f_1(\vec{p}) d^3\vec{p}\right)\left(A\ v_x\ \delta t\right) \quad . \tag{III.62}$$

The final factor in the above expression is the volume of a cylinder of height $v_x \delta t$ perpendicular to the area element A. Only particles within this cylinder are close enough to impact the wall during δt. As each collision imparts a momentum $2p_x$ to the wall, the net force exerted is

$$F = \frac{1}{\delta t} \int_{-\infty}^{0} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z f_1(\vec{p}) \left(A \, \frac{p_x}{m} \, \delta t \right) (2p_x). \tag{III.63}$$

As only particles with velocities directed towards the wall will hit it, the first integral is over half of the range of p_x. Since the integrand is even in p_x, this restriction can be removed by dividing the full integral by 2. The pressure P is then obtained from the force per unit area as

$$P = \frac{F}{A} = \int d^3\vec{p} \; f_1(\vec{p}) \frac{p_x^2}{m} = \frac{1}{m} \int d^3\vec{p} \; p_x^2 \; n \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp\left(-\frac{\beta p^2}{2m} \right) = \frac{n}{\beta} \quad , \tag{III.64}$$

where eq.(III.56) is used for the equilibrium form of f_1. Comparing with the standard equation of state, $PV = Nk_BT$, for an ideal gas, leads to the identification, $\beta = 1/k_BT$.

(4) *Entropy:* As discussed earlier, the Boltzmann H-function is closely related to the information content of the one-particle PDF ρ_1. We can also define a corresponding Boltzmann entropy,

$$S_B(t) = -k_B \mathrm{H}(t), \tag{III.65}$$

where the constant k_B reflects the historical origins of entropy. The H-theorem implies that S_B can only increase with time in approaching equilibrium. It has the further advantage of being defined through eq.(III.42) for situations that are clearly out of equilibrium. For a gas in equilibrium in a box of volume V, from eq.(III.56), we compute

$$\begin{aligned} \mathrm{H} &= V \int d^3\vec{p} \; f_1(\vec{p}) \ln f_1(\vec{p}) \\ &= V \int d^3\vec{p} \; \frac{N}{V} (2\pi m k_B T)^{-3/2} \exp\left(-\frac{p^2}{2mk_BT} \right) \left[\ln\left(\frac{n}{(2\pi m k_B T)^{3/2}} \right) - \frac{p^2}{2mk_BT} \right] \\ &= N \left[\ln\left(\frac{n}{(2\pi m k_B T)^{3/2}} \right) - \frac{3}{2} \right]. \end{aligned} \tag{III.66}$$

The entropy is now identified as

$$S_B = -k_B \mathrm{H} = N k_B \left[\frac{3}{2} + \frac{3}{2} \ln\left(2\pi m k_B T \right) - \ln\left(\frac{N}{V} \right) \right]. \tag{III.67}$$

The thermodynamic relation, $TdS_B = dE + PdV$, implies

$$\begin{aligned} \left.\frac{\partial E}{\partial T}\right|_V &= T \left.\frac{\partial S_B}{\partial T}\right|_V = \frac{3}{2} N k_B, \\ P + \left.\frac{\partial E}{\partial V}\right|_T &= T \left.\frac{\partial S_B}{\partial V}\right|_T = \frac{N k_B T}{V} \quad . \end{aligned} \tag{III.68}$$

The usual properties of a monatomic ideal gas, $PV = Nk_BT$, and $E = 3Nk_BT/2$, can now be obtained from the above equations. Also note that for this classical gas, the zero temperature limit of the entropy in eq.(III.67) *is not* independent of the density n, in violation of the third law of thermodynamics.

III.G Conservation Laws

• *Approach to equilibrium:* We now address the third question posed in the introduction, of *how* the gas reaches its final equilibrium. Consider a situation in which the gas is perturbed from the equilibrium form described by eq.(III.56), and follow its relaxation to equilibrium. There is a hierarchy of mechanisms that operate at different time scales.

(i) The fastest processes are the two body collisions of particles in immediate vicinity. Over a time scale of the order of τ_c, $f_2(\vec{q}_1, \vec{q}_2, t)$ relaxes to $f_1(\vec{q}_1, t) f_1(\vec{q}_2, t)$ for separations $|\vec{q}_1 - \vec{q}_2| \gg d$. Similar relaxations occur for the higher order densities f_s.

(ii) At the next stage, f_1 relaxes to a *local equilibrium* from, as in eq.(III.53), over the time scale of the mean free time $\tau_\times$. This is the intrinsic scale set by the collision term on the right hand side of the Boltzmann equation. After this time interval, quantities conserved in collisions achieve a state of local equilibrium. We can then define at each point a (time dependent) local density by integrating over all momenta as

$$n(\vec{q}, t) = \int d^3\vec{p} f_1(\vec{p}, \vec{q}, t), \tag{III.69}$$

as well as a local expectation value for any operator $\mathcal{O}(\vec{p}, \vec{q}, t)$

$$\langle \mathcal{O}(\vec{q}, t) \rangle = \frac{1}{n(\vec{q}, t)} \int d^3\vec{p} f_1(\vec{p}, \vec{q}, t) \mathcal{O}(\vec{p}, \vec{q}, t). \tag{III.70}$$

(iii) After the densities and expectation values have relaxed to their local equilibrium forms in the intrinsic time scales τ_c and $\tau_\times$, there is a subsequent slower relaxation to global equilibrium over extrinsic time and length scales. This final stage is governed by the smaller streaming terms on the left hand side of the Boltzmann equation. It is most conveniently expressed in terms of the time evolution of conserved quantities according to *hydrodynamic equations*.

Conserved quantities are left unchanged by the two body collisions, i.e. satisfy

$$\chi(\vec{p}_1, \vec{q}, t) + \chi(\vec{p}_2, \vec{q}, t) = \chi(\vec{p}_1\,', \vec{q}, t) + \chi(\vec{p}_2\,', \vec{q}, t), \tag{III.71}$$

where $(\vec{p}_1, \vec{p}_2)$ and $(\vec{p}_1\,', \vec{p}_2\,')$ refer to the momenta before and after a collision, respectively. For such quantities, we have

$$J_\chi(\vec{q}, t) = \int d^3\vec{p} \chi(\vec{p}, \vec{q}, t) \left. \frac{df_1}{dt} \right|_{\rm coll.} (\vec{p}, \vec{q}, t) = 0. \tag{III.72}$$

- **Proof:** Using the form of the collision integral, we have

$$J_\chi = -\int d^3\vec{p}_1 d^3\vec{p}_2 d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|\,[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')]\,\chi(\vec{p}_1). \tag{III.73}$$

(The implicit arguments $(\vec{q},t)$ are left out for ease of notation.) We now perform the same set of changes of variables that were used in the proof of the H-theorem. The first step is averaging after exchange of the dummy variables $\vec{p}_1$ and $\vec{p}_2$, leading to

$$J_\chi = -\frac{1}{2}\int d^3\vec{p}_1 d^3\vec{p}_2 d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|\,[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')]\,[\chi(\vec{p}_1) + \chi(\vec{p}_2)]\,. \tag{III.74}$$

Next, change variables from the originators $(\vec{p}_1,\vec{p}_2,\vec{b}\,)$, to the products $(\vec{p}_1\,',\vec{p}_2\,',\vec{b}\,')$ of the collision. After relabeling the integration variables, the above equation is transformed to

$$J_\chi = -\frac{1}{2}\int d^3\vec{p}_1 d^3\vec{p}_2 d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|\,[f_1(\vec{p}_1\,')f_1(\vec{p}_2\,') - f_1(\vec{p}_1)f_1(\vec{p}_2)]\,[\chi(\vec{p}_1\,') + \chi(\vec{p}_2\,')]\,. \tag{III.75}$$

Averaging the last two equations leads to

$$\begin{aligned} J_\chi = -\frac{1}{4}\int d^3\vec{p}_1 d^3\vec{p}_2 d^2\vec{b}\,|\vec{v}_1 - \vec{v}_2|\,&[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1\,')f_1(\vec{p}_2\,')] \\ &[\chi(\vec{p}_1) + \chi(\vec{p}_2) - \chi(\vec{p}_1\,') - \chi(\vec{p}_2\,')]\,, \end{aligned} \tag{III.76}$$

which is zero from eq.(III.71).

Let us explore the consequences of this result for the evolution of expectation values involving χ. Substituting for the collision term in eq.(III.72) the streaming terms on the left hand side of the Boltzmann equation, leads to

$$J_\chi(\vec{q},t) = \int d^3\vec{p}\,\chi(\vec{p},\vec{q},t)\left[\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha\frac{\partial}{\partial p_\alpha}\right] f_1(\vec{p},\vec{q},t) = 0, \tag{III.77}$$

where we have introduced the notations $\partial_t \equiv \partial/\partial t$, $\partial_\alpha \equiv \partial/\partial q_\alpha$, and $F_\alpha = -\partial U/\partial q_\alpha$. We can manipulate the above equation into the form

$$\int d^3\vec{p}\left\{\left[\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha\frac{\partial}{\partial p_\alpha}\right](\chi f_1) - f_1\left[\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha\frac{\partial}{\partial p_\alpha}\right]\chi\right\} = 0. \tag{III.78}$$

The third term is zero, as it is a complete derivative. Using the definition of expectation values in eq.(III.70), the remaining terms can be rearranged into

$$\partial_t\left(n\langle\chi\rangle\right) + \partial_\alpha\left(n\left\langle\frac{p_\alpha}{m}\chi\right\rangle\right) - n\langle\partial_t\chi\rangle - n\left\langle\frac{p_\alpha}{m}\partial_\alpha\chi\right\rangle - nF_\alpha\left\langle\frac{\partial\chi}{\partial p_\alpha}\right\rangle = 0. \tag{III.79}$$

As discussed earlier, for elastic collisions, there are 5 conserved quantities: particle number, the three components of momentum, and kinetic energy. Each leads to a corresponding hydrodynamic equation, as constructed below:

(a) *Particle number:* Setting $\chi = 1$ in eq.(III.79) leads to

$$\partial_t n + \partial_\alpha \left(n u_\alpha \right) = 0, \tag{III.80}$$

where we have introduced the local velocity

$$\vec{u} \equiv \left\langle \frac{\vec{p}}{m} \right\rangle . \tag{III.81}$$

This equation simply states that the time variation of the local particle density is due to a particle current $\vec{J}_n = n\vec{u}$.

(b) *Momentum:* Any linear function of the momentum $\vec{p}$ is conserved in the collision, and we shall explore the consequences of the conservation of

$$\vec{c} \equiv \frac{\vec{p}}{m} - \vec{u}. \tag{III.82}$$

Substituting c_α into eq.(III.79) leads to

$$\partial_\beta \left(n \left\langle \left(u_\beta + c_\beta \right) c_\alpha \right\rangle \right) + n \partial_t u_\alpha + n \partial_\beta u_\alpha \left\langle u_\beta + c_\beta \right\rangle - n \frac{F_\alpha}{m} = 0. \tag{III.83}$$

Taking advantage of $\langle c_\alpha \rangle = 0$, from eqs.(III.81) and (III.82), leads to

$$\partial_t u_\alpha + u_\beta \partial_\beta u_\alpha = \frac{F_\alpha}{m} - \frac{1}{mn} \partial_\beta P_{\alpha\beta} \, , \tag{III.84}$$

where we have introduced the *pressure tensor*,

$$P_{\alpha\beta} \equiv mn \left\langle c_\alpha c_\beta \right\rangle . \tag{III.85}$$

The left hand side of the equation is the acceleration of an element of the fluid $d\vec{u}/dt$, which should equal $\vec{F}_{\rm net}/m$ according to Newton's equation. The net force includes an additional component due to the variations in the pressure tensor across the fluid.

(c) *Kinetic energy:* We first introduce an average local kinetic energy

$$\varepsilon \equiv \left\langle \frac{mc^2}{2} \right\rangle = \left\langle \frac{p^2}{2m} - \vec{p} \cdot \vec{u} + \frac{mu^2}{2} \right\rangle , \tag{III.86}$$

and then examine the conservation law obtained by setting χ equal to $mc^2/2$ in eq.(III.79). Since for space and time derivatives $\partial\varepsilon = mc_\beta \partial c_\beta = -mc_\beta \partial u_\beta$, we obtain

$$\partial_t(n\varepsilon) + \partial_\alpha \left(n \left\langle (u_\alpha + c_\alpha) \frac{mc^2}{2} \right\rangle \right) + nm\partial_t u_\beta \langle c_\beta \rangle + nm\partial_\alpha u_\beta \langle (u_\alpha + c_\alpha) c_\beta \rangle - nF_\alpha \langle c_\alpha \rangle = 0. \tag{III.87}$$

Taking advantage of $\langle c_\alpha \rangle = 0$, the above equation is simplified to

$$\partial_t(n\varepsilon) + \partial_\alpha (nu_\alpha \varepsilon) + \partial_\alpha \left(n \left\langle c_\alpha \frac{mc^2}{2} \right\rangle \right) + P_{\alpha\beta}\partial_\alpha u_\beta = 0. \tag{III.88}$$

We next take out the dependence on n in the first two terms of the above equation, finding

$$\varepsilon\partial_t n + n\partial_t\varepsilon + \varepsilon\partial_\alpha (nu_\alpha) + nu_\alpha\partial_\alpha\varepsilon + \partial_\alpha h_\alpha + P_{\alpha\beta}u_{\alpha\beta} = 0, \tag{III.89}$$

where we have also introduced the local *heat flux*

$$\vec{h} \equiv \frac{nm}{2} \left\langle c_\alpha c^2 \right\rangle, \tag{III.90}$$

and the *rate of strain tensor*

$$u_{\alpha\beta} = \frac{1}{2} \left(\partial_\alpha u_\beta + \partial_\beta u_\alpha \right). \tag{III.91}$$

Eliminating the first and third terms in eq.(III.89) with the aid of eq.(III.80) leads to

$$\partial_t\varepsilon + u_\alpha\partial_\alpha\varepsilon = -\frac{1}{n}\partial_\alpha h_\alpha - \frac{1}{n}P_{\alpha\beta}u_{\alpha\beta}. \tag{III.92}$$

Clearly to solve the hydrodynamic equations for n, $\vec{u}$, and ε, we need expressions for $P_{\alpha\beta}$ and $\vec{h}$, which are either given phenomenologically, or calculated from the density f_1, as in the next sections.

III.H Zeroth Order Hydrodynamics

As a first approximation, we shall assume that in *local equilibrium*, the density f_1 at each point in space can be represented as in eq.(III.56), i.e.

$$f_1^0(\vec{p},\vec{q},t) = \frac{n(\vec{q},t)}{\left(2\pi m k_B T(\vec{q},t)\right)^{3/2}} \exp\left[-\frac{\left(\vec{p}-m\vec{u}(\vec{q},t)\right)^2}{2mk_BT(\vec{q},t)}\right]. \tag{III.93}$$

The choice of parameters clearly enforces $\int d^3\vec{p}\, f_1^0 = n$, and $\langle \vec{p}/m\rangle^0 = \vec{u}$, as required. Average values are easily calculated from this Gaussian weight; in particular

$$\langle c_\alpha c_\beta\rangle^0 = \frac{k_BT}{m}\delta_{\alpha\beta}\,, \tag{III.94}$$

leading to

$$P^0_{\alpha\beta} = nk_BT\delta_{\alpha\beta}\,, \qquad \text{and} \qquad \varepsilon = \frac{3}{2}k_BT. \tag{III.95}$$

Since the density f_1^0 is even in $\vec{c}$, all odd expectation values vanish, and in particular

$$\vec{h}^0 = 0. \tag{III.96}$$

The conservation laws in this approximation take the simple forms

$$\begin{cases} D_t n = -n\partial_\alpha u_\alpha \\ mD_t u_\alpha = F_\alpha - \dfrac{1}{n}\partial_\alpha\left(nk_BT\right) \\ D_t T = -\dfrac{2}{3}T\partial_\alpha u_\alpha \end{cases}. \tag{III.97}$$

In the above expression, we have introduced the *material derivative*

$$D_t \equiv \left[\partial_t + u_\beta\partial_\beta\right], \tag{III.98}$$

which measures the time variations of any quantity as it moves along the stream-lines set up by the average velocity field $\vec{u}$. By combining the first and third equations, it is easy to get

$$D_t \ln\left(nT^{-3/2}\right) = 0. \tag{III.99}$$

The quantity $\ln\left(nT^{-3/2}\right)$ is like a local entropy for the gas (see eq.(III.67)), which according to the above equation is not changed along stream-lines. The zeroth order hydrodynamics thus predicts that the gas flow is adiabatic. This prevents the local equilibrium solution

of eq.(III.93) from reaching a true global equilibrium form which necessitates an increase in entropy.

To demonstrate that eqs.(III.97) do not describe a satisfactory approach to equilibrium, examine the evolution of small deformations about a stationary ($\vec{u}_0 = 0$) state, in a uniform box ($\vec{F} = 0$), by setting

$$\begin{cases} n(\vec{q},t) = \overline{n} + \nu(\vec{q},t) \\ T(\vec{q},t) = \overline{T} + \theta(\vec{q},t) \end{cases} . \tag{III.100}$$

We shall next expand eqs.(III.97) to *first order* in the deviations $(\nu, \theta, \vec{u})$. Note that to lowest order, $D_t = \partial_t + O(u)$, leading to the linearized zeroth order hydrodynamic equations

$$\begin{cases} \partial_t \nu = -\overline{n}\partial_\alpha u_\alpha \\ m\partial_t u_\alpha = -\dfrac{k_B\overline{T}}{\overline{n}}\partial_\alpha \nu - k_B\partial_\alpha\theta \\ \partial_t\theta = -\dfrac{2}{3}\overline{T}\partial_\alpha u_\alpha \end{cases} . \tag{III.101}$$

- *Normal modes* of the system are obtained by Fourier transformations,

$$A\left(\vec{k},\omega\right) = \int d^3\vec{q}\,dt\, \exp\left[i\left(\vec{k}\cdot\vec{q} - \omega t\right)\right] A\left(\vec{q},t\right), \tag{III.102}$$

where A stands for any of the three fields $(\nu, \theta, \vec{u})$. The natural vibration frequencies are solutions to the matrix equation

$$\omega \begin{pmatrix} \nu \\ u_\alpha \\ \theta \end{pmatrix} = \begin{pmatrix} 0 & \overline{n}k_\beta & 0 \\ \frac{k_B\overline{T}}{m\overline{n}}\delta_{\alpha\beta}k_\beta & 0 & \frac{k_B}{m}\delta_{\alpha\beta}k_\beta \\ 0 & \frac{2}{3}\overline{T}k_\beta & 0 \end{pmatrix} \begin{pmatrix} \nu \\ u_\beta \\ \theta \end{pmatrix} . \tag{III.103}$$

It is easy to check that this equation has the following modes, the first *three* with zero frequency:

(a) Two modes describe shear flows in a uniform ($n = \overline{n}$) and isothermal ($T = \overline{T}$) fluid, in which the velocity varies along a direction normal to its orientation (e.g. $\vec{u} = f(x,t)\hat{y}$). In terms of Fourier modes $\vec{k}\cdot\vec{u}_T(\vec{k}\,) = 0$, indicating *transverse* flows that are not relaxed in this zeroth order approximation.

(b) A third zero frequency mode describes a stationary fluid with *uniform pressure* $P = nk_BT$. While n and T may vary across space, their product is constant, insuring

that the fluid will not start moving due to pressure variations. The corresponding eigenvector of eq.(III.103) is

$$\mathbf{v_e} = \begin{pmatrix} \overline{n} \\ 0 \\ -\overline{T} \end{pmatrix}. \tag{III.104}$$

(c) Finally, the *longitudinal* velocity ($\vec{u}_\ell \parallel \vec{k}$) combines with density and temperature variations in eigenmodes of the form

$$\mathbf{v_l} = \begin{pmatrix} \overline{n}|\vec{k}| \\ \omega(\vec{k}) \\ \frac{2}{3}\overline{T}|\vec{k}| \end{pmatrix}, \qquad \text{with} \qquad \omega(\vec{k}) = \pm v_\ell |\vec{k}|, \tag{III.105}$$

where

$$v_\ell = \sqrt{\frac{5}{3}\frac{k_B\overline{T}}{m}}, \tag{III.106}$$

is the longitudinal sound velocity. Note that the density and temperature variations in this mode are *adiabatic*, i.e. the local entropy (proportional to $\ln\left(nT^{-3/2}\right)$) is left unchanged.

We thus find that none of the conserved quantities relaxes to equilibrium in the zeroth order approximation. Shear flow and entropy modes persist forever, while the two sound modes have undamped oscillations. This is a deficiency of the zeroth order approximation which is removed by finding a better solution to the Boltzmann equation.

III.I First Order Hydrodynamics

While $f_1^0(\vec{p},\vec{q},t)$ of eq.(III.93) does set the right hand side of the Boltzmann equation to zero, it is not a full solution, as the left hand side causes its form to vary. The left hand side is a *linear* differential operator, which using the various notations introduced in the previous sections, can be written as

$$\mathcal{L}[f] \equiv \left[\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha\frac{\partial}{\partial p_\alpha}\right] f = \left[D_t + c_\alpha\partial_\alpha + \frac{F_\alpha}{m}\frac{\partial}{\partial c_\alpha}\right] f. \tag{III.107}$$

It is simpler to examine the effect of $\mathcal{L}$ on $\ln f_1^0$. which can be written as

$$\ln f_1^0 = \ln\left(nT^{-3/2}\right) - \frac{mc^2}{2k_BT} - \frac{3}{2}\ln\left(2\pi m k_B\right). \tag{III.108}$$

Using the relation $\partial(c^2/2) = c_\beta \partial c_\beta = -c_\beta \partial u_\beta$, we get

$$\begin{aligned}\mathcal{L}\left[\ln f_1^0\right] =& D_t \ln\left(nT^{-3/2}\right) + \frac{mc^2}{2k_BT^2} D_t T + \frac{m}{k_BT} c_\alpha D_t u_\alpha \\ &+ c_\alpha \left(\frac{\partial_\alpha n}{n} - \frac{3}{2}\frac{\partial_\alpha T}{T}\right) + \frac{mc^2}{2k_BT^2} c_\alpha \partial_\alpha T + \frac{m}{k_BT} c_\alpha c_\beta \partial_\alpha u_\beta - \frac{F_\alpha c_\alpha}{k_BT}.\end{aligned} \tag{III.109}$$

If the fields n, T, and u_α, satisfy the zeroth order hydrodynamic eqs.(III.97), we can simplify the above equation to

$$\begin{aligned}\mathcal{L}\left[\ln f_1^0\right] =& 0 - \frac{mc^2}{3k_BT}\partial_\alpha u_\alpha + c_\alpha \left[\left(\frac{F_\alpha}{k_BT} - \frac{\partial_\alpha n}{n} - \frac{\partial_\alpha T}{T}\right) + \left(\frac{\partial_\alpha n}{n} - \frac{3}{2}\frac{\partial_\alpha T}{T}\right) - \frac{F_\alpha}{k_BT}\right] \\ &+ \frac{mc^2}{2k_BT^2} c_\alpha \partial_\alpha T + \frac{m}{k_BT} c_\alpha c_\beta u_{\alpha\beta} \\ =& \frac{m}{k_BT}\left(c_\alpha c_\beta - \frac{\delta_{\alpha\beta}}{3}c^2\right) u_{\alpha\beta} + \left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right)\frac{c_\alpha}{T}\partial_\alpha T.\end{aligned} \tag{III.110}$$

The characteristic time scale τ_U for $\mathcal{L}$ is *extrinsic*, and can be made much larger than $\tau_\times$. The zeroth order result is thus exact in the limit $(\tau_\times/\tau_U) \to 0$; and corrections can be constructed in a perturbation series in $(\tau_\times/\tau_U)$. To this purpose, we set $f_1 = f_1^0(1+g)$, and linearize the collision operator as

$$\begin{aligned}C\left[f_1, f_1\right] =& -\int d^3\vec{p}_2 d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2| f_1^0(\vec{p}_1) f_1^0(\vec{p}_2) \left[g(\vec{p}_1) + g(\vec{p}_2) - g(\vec{p}_1\,') - g(\vec{p}_2\,')\right] \\ \equiv& -f_1^0(\vec{p}_1) C_L[g].\end{aligned} \tag{III.111}$$

While linear, the above integral operator is still difficult to manipulate in general. As a first approximation, and noting its characteristic magnitude, we set

$$C_L[g] \approx \frac{g}{\tau_\times}. \tag{III.112}$$

This is known as the *single collision time* approximation, and from the linearized Boltzmann equation $\mathcal{L}[f_1] = -f_1^0 C_L[g]$, we obtain

$$g = -\tau_\times \frac{1}{f_1^0}\mathcal{L}\left[f_1\right] \approx -\tau_\times \mathcal{L}\left[\ln f_1^0\right], \tag{III.113}$$

where we have kept only the leading term. Thus the first order solution is given by (using eq.(III.110))

$$f_1^1(\vec{p},\vec{q},t) = f_1^0(\vec{p},\vec{q},t)\left[1 - \frac{\tau_\mu m}{k_BT}\left(c_\alpha c_\beta - \frac{\delta_{\alpha\beta}}{3}c^2\right) u_{\alpha\beta} - \tau_K \left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right)\frac{c_\alpha}{T}\partial_\alpha T\right], \tag{III.114}$$

where $\tau_\mu = \tau_K = \tau_\times$ in the single collision time approximation. However, in writing the above equation, we have anticipated the possibility of $\tau_\mu \neq \tau_K$ which arises in more sophisticated treatments (although both times are still of order of $\tau_\times$).

It is easy to check that $\int d^3\vec{p} f_1^1 = \int d^3\vec{p} f_1^0 = n$, and thus various local expectation values are calculated to first order as

$$\langle \mathcal{O} \rangle^1 = \frac{1}{n} \int d^3\vec{p} \mathcal{O} f_1^0 (1+g) = \langle \mathcal{O} \rangle^0 + \langle g\mathcal{O} \rangle^0 . \tag{III.115}$$

The calculation of averages over products of c_α's, distributed according to the Gaussian weight of f_1^0, is greatly simplified by the use of *Wick's theorem*, which states that expectation value of the product is the sum over all possible products of paired expectation values, for example

$$\langle c_\alpha c_\beta c_\gamma c_\delta \rangle_0 = \left(\frac{k_B T}{m} \right)^2 (\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) . \tag{III.116}$$

(Expectation values involving a product of an odd number of c_α's are zero by symmetry.) Using this result, it is easy to verify that

$$\left\langle \frac{p_\alpha}{m} \right\rangle^1 = u_\alpha - \tau_K \frac{\partial_\beta T}{T} \left\langle \left(\frac{mc^2}{2k_B T} - \frac{5}{2} \right) c_\alpha c_\beta \right\rangle^0 = u_\alpha . \tag{III.117}$$

The pressure tensor at first order is given by

$$\begin{aligned} P^1_{\alpha\beta} =& nm \langle c_\alpha c_\beta \rangle^1 = nm \left[\langle c_\alpha c_\beta \rangle^0 - \frac{\tau_\mu m}{k_B T} \left\langle c_\alpha c_\beta \left(c_\mu c_\nu - \frac{\delta_{\mu\nu}}{3} c^2 \right) \right\rangle^0 u_{\mu\nu} \right] \\ =& nk_B T \delta_{\alpha\beta} - 2nk_B T \tau_\mu \left(u_{\alpha\beta} - \frac{\delta_{\alpha\beta}}{3} u_{\gamma\gamma} \right) . \end{aligned} \tag{III.118}$$

(Using the above result, we can further verify that $\varepsilon^1 = \langle mc^2/2 \rangle^1 = 3k_B T/2$, as before.) Finally, the heat flux is given by

$$\begin{aligned} h^1_\alpha =& n \left\langle c_\alpha \frac{mc^2}{2} \right\rangle^1 = -\frac{nm\tau_K}{2} \frac{\partial_\beta T}{T} \left\langle \left(\frac{mc^2}{2k_B T} - \frac{5}{2} \right) c_\alpha c_\beta c^2 \right\rangle^0 \\ =& -\frac{5}{2} \frac{nk_B^2 T \tau_K}{m} \partial_\alpha T . \end{aligned} \tag{III.119}$$

At this order, we find that spatial variations in temperature generate a heat flow that tends to smooth them out, while shear flows are opposed by the off-diagonal terms in the pressure tensor. These effects are sufficient to cause relaxation to equilibrium, as can be seen by examining the modified behavior of the modes discussed previously.

(a) The pressure tensor now has an off–diagonal term

$$P^1_{\alpha\neq\beta} = -2nk_BT\tau_\mu u_{\alpha\beta} \equiv -\mu\left(\partial_\alpha u_\beta + \partial_\beta u_\alpha\right), \tag{III.120}$$

where $\mu \equiv nk_BT\tau_\mu$ is the *viscosity coefficient*. A shearing of the fluid (e.g. described by a velocity $u_y(x,t)$) now leads to a a viscous force that opposes it (proportional to $\mu\partial_x^2 u_y$), causing its diffusive relaxation as discussed below.

(b) Similarly, a temperature gradient leads to a heat flux

$$\vec{h} = -K\nabla T, \tag{III.121}$$

where $K = (5nk_B^2T\tau_K)/(2m)$ is the coefficient of *thermal conductivity* of the gas. If the gas is at rest ($\vec{u} = 0$, and uniform $P = nk_BT$), variations in temperature now satisfy

$$n\partial_t\varepsilon = \frac{3}{2}nk_B\partial_t T = -\partial_\alpha\left(-K\partial_\alpha T\right), \quad \Rightarrow \quad \partial_t T = \frac{2K}{3nk_B}\nabla^2 T. \tag{III.122}$$

This is the *Fourier equation* and shows that temperature variations relax by diffusion.

We can discuss the behavior of all the modes by linearizing the equations of motion. The first order contribution to $D_t u_\alpha \approx \partial_t u_\alpha$ is

$$\delta^1\left(\partial_t u_\alpha\right) \equiv \frac{1}{mn}\partial_\beta\delta^1 P_{\alpha\beta} \approx -\frac{\mu}{m\overline{n}}\left(\frac{1}{3}\partial_\alpha\partial_\beta + \delta_{\alpha\beta}\partial_\gamma\partial_\gamma\right)u_\beta, \tag{III.123}$$

where $\mu \equiv \overline{n}k_B\overline{T}\tau_\mu$. Similarly, the correction for $D_tT \approx \partial_t\theta$, is given by

$$\delta^1\left(\partial_t\theta\right) \equiv -\frac{2}{3k_Bn}\partial_\alpha h_\alpha \approx -\frac{2K}{3k_B\overline{n}}\partial_\alpha\partial_\alpha\theta, \tag{III.124}$$

with $K = (5\overline{n}k_B^2\overline{T}\tau_K)/(2m)$. After Fourier transformation, the matrix equation (III.103) is modified to

$$\omega\begin{pmatrix}\nu\\ u_\alpha\\ \theta\end{pmatrix} = \begin{pmatrix} 0 & \overline{n}\delta_{\alpha\beta}k_\beta & 0\\ \frac{k_B\overline{T}}{m\overline{n}}\delta_{\alpha\beta}k_\beta & -i\frac{\mu}{m\overline{n}}\left(k^2\delta_{\alpha\beta} + \frac{k_\alpha k_\beta}{3}\right) & \frac{k_B}{m}\delta_{\alpha\beta}k_\beta\\ 0 & \frac{2}{3}\overline{T}\delta_{\alpha\beta}k_\beta & -i\frac{2Kk^2}{3k_B\overline{n}}\end{pmatrix}\begin{pmatrix}\nu\\ u_\beta\\ \theta\end{pmatrix}. \tag{III.125}$$

We can ask how the normal mode frequencies calculated in the zeroth order approximation are modified at this order. It is simple to verify that the transverse (shear) normal models ($\vec{k}\cdot\vec{u}_T = 0$) now have a frequency

$$\omega_T = -i\frac{\mu}{m\overline{n}}k^2. \tag{III.126}$$

The imaginary frequency implies that these modes are damped over a characteristic time $\tau_T(k) \sim 1/|\omega_T| \sim (\lambda)^2/(\tau_\mu \overline{v}^2)$, where λ is the corresponding wavelength, and $\overline{v} \sim \sqrt{k_B T/m}$ is a typical gas particle velocity. We see that the characteristic time scales grow as the square of the wavelength, which is characteristic of *diffusive* processes.

In the remaining normal modes the velocity is parallel to $\vec{k}$, and eq.(III.125) reduces to

$$\omega \begin{pmatrix} \nu \\ u_\ell \\ \theta \end{pmatrix} = \begin{pmatrix} 0 & \overline{n}k & 0 \\ \frac{k_B \overline{T}}{m\overline{n}}k & -i\frac{4\mu k^2}{3m\overline{n}} & \frac{k_B}{m}k \\ 0 & \frac{2}{3}\overline{T}k & -i\frac{2Kk^2}{3k_B\overline{n}} \end{pmatrix} \begin{pmatrix} \nu \\ u_\beta \\ \theta \end{pmatrix}. \tag{III.127}$$

The determinant of the dynamical matrix is the product of the three eigen-frequencies, and to lowest order is given by

$$\det(M) = i\frac{2Kk^2}{3k_B\overline{n}} \cdot \overline{n}k \cdot \frac{k_B\overline{T}k}{m\overline{n}} + \mathcal{O}(\tau_\times^2). \tag{III.128}$$

At zeroth order the two sound modes have $\omega_\pm^0(k) = \pm v_\ell k$, and hence the frequency of the isobaric mode is

$$\omega_e^1(k) \approx \frac{\det(M)}{-v_\ell^2 k^2} = -i\frac{2Kk^2}{5k_B\overline{n}} + \mathcal{O}(\tau_\times^2). \tag{III.129}$$

At first order, the longitudinal sound modes also turn into damped oscillations with frequencies $\omega_\pm^1(k) = \pm v_\ell k - i\gamma$. The simplest way to obtain the decay rates is to note that the trace of the dynamical matrix is equal to the sum of the eigenvalues, and hence

$$\omega_\pm^1(k) = \pm v_\ell k - ik^2\left(\frac{2\mu}{3m\overline{n}} + \frac{2K}{15k_B\overline{n}}\right) + \mathcal{O}(\tau_\times^2). \tag{III.130}$$

The damping of all normal modes guarantees the, albeit slow, approach of the gas to its final uniform and stationary equilibrium state.

IV. Classical Statistical Mechanics

IV.A General Definitions

• **Statistical Mechanics** *is a probabilistic approach to equilibrium macroscopic properties of large numbers of degrees of freedom.*

As discussed in chapter I, equilibrium properties of macroscopic bodies are phenomenologically described by the laws of thermodynamics. The macro-state M, depends on a relatively small number of thermodynamic coordinates. To provide a more fundamental derivation of these properties, we can examine the dynamics of the many degrees of freedom N, comprising a macroscopic body. Description of each micro-state μ, requires an enormous amount of information, and the corresponding time evolution, governed by the Hamiltonian equations (discussed in chapter II), is usually quite complicated. Rather than following the evolution of an individual (pure) micro-state, statistical mechanics examines an ensemble of micro-states corresponding to a given (mixed) macro-state. It aims to provide the probabilities $p_M(\mu)$, for the equilibrium ensemble. Liouville's theorem justifies the assumption that all accessible micro-states are equally likely in an equilibrium ensemble. As discussed in chapter III, such assignment of probabilities is subjective. In this chapter we shall provide unbiased estimates of $p_M(\mu)$ for a number of different equilibrium ensembles. A central conclusion is that in the thermodynamic limit of large N all these ensembles are in fact equivalent. In contrast to kinetic theory, equilibrium statistical mechanics leaves out the question of how various systems achieve equilibrium.

IV.B The Microcanonical Ensemble

Our starting point in thermodynamics is a mechanically and adiabatically isolated system. In the absence of heat or work input to the system, the internal energy E, and the generalized coordinates $\mathbf{x}$, are fixed, specifying a macro-state $M \equiv (E, \mathbf{x})$. The corresponding set of mixed micro-states form the *microcanonical ensemble*. In classical statistical mechanics, these microstates are defined by points in phase space, their time evolution governed by a Hamiltonian $\mathcal{H}(\mu)$, as discussed in Chapter II. Since the Hamiltonian equations (II.1) conserve the total energy of a given system, all micro-states are confined to the surface $\mathcal{H}(\mu) = E$ in phase space. Assume that there are no other conserved quantities, so

that all points on this surface are mutually accessible. The central postulate of statistical mechanics is that the equilibrium probability distribution is given by

$$p_{(E,\mathbf{x})}(\mu) = \frac{1}{\Omega(E,\mathbf{x})} \cdot \begin{cases} 1 & \text{for } \mathcal{H}(\mu) = E \\ \\ 0 & \text{otherwise} \end{cases} . \tag{IV.1}$$

Some remarks and clarification on the above postulate are in order:

(1) *Boltzmann's assumption of equal a priori equilibrium probabilities* refers to the above postulate, which is in fact the unbiased probability estimate in phase space subject to the constraint of constant energy. This assignment is consistent with, but not required by, Liouville's theorem. Note that the phase space, specifying the microstates μ, must be composed of *canonically conjugate pairs*. Under a *canonical* change of variables, $\mu \to \mu'$, volumes in phase space are left invariant. The Jacobian of such transformations is unity, and the transformed probability, $p(\mu') = p(\mu)\,|\partial\mu/\partial\mu'|$, is again uniform on the surface of constant energy.

(2) *The normalization factor* $\Omega(E,\mathbf{x})$, is the area of the surface of constant energy E in phase space. To avoid subtleties associated with densities that are non-zero only a surface, is sometimes more convenient to define the microcanonical ensemble by requiring $E - \Delta \leq \mathcal{H}(\mu) \leq E + \Delta$, i.e. assigning the energy of the ensemble up to an uncertainty of Δ. In this case, the accessible phase space forms a shell of thickness Δ around the surface of energy E. The normalization is now the volume of the shell, $\Omega' \approx 2\Delta\Omega$. Since Ω typically depends exponentially on E, as long as $\Delta \sim \mathcal{O}(E^0)$ (or even $\mathcal{O}(E^1)$), the difference between the surface and volume of the shell is negligible in the $E \propto N \to \infty$ limit, and we shall use Ω and Ω' interchangeably.

(3) *The entropy* of this uniform probability distribution is given by

$$S(E,\mathbf{x}) = k_B \ln \Omega(E,\mathbf{x}). \tag{IV.2}$$

An additional factor of k_B is introduced compared to the definition of eq.(III.68), so that the entropy has the correct dimensions of energy per degrees Kelvin, used in thermodynamics. Ω and S are not changed by a canonical change of coordinates in phase space. For a collection of independent systems, the overall allowed phase space is the product of individual ones, i.e. $\Omega_{\text{Total}} = \prod_i \Omega_i$. The resulting entropy is thus additive, as expected for an extensive quantity.

Various results in thermodynamics now follow from eq.(IV.1), provided that we consider macroscopic systems with many degrees of freedom.

• *The Zeroth law:* Equilibrium properties are discussed in thermodynamics by placing two previously isolated systems in contact, and allowing them to exchange heat. We can similarly bring together two microcanonical systems, and allowing them to exchange energy, but not work. If the original systems have energies E_1 and E_2 respectively, the combined system has energy $E = E_1 + E_2$. Assuming that interactions between the two parts are small, each micro-state of the joint system corresponds to a pair of micro-states of the two components, i.e. $\mu = \mu_1 \otimes \mu_2$, and $\mathcal{H}(\mu_1 \otimes \mu_2) = \mathcal{H}_1(\mu_1) + \mathcal{H}_2(\mu_2)$. As the joint system is in a microcanonical ensemble of energy $E = E_1 + E_2$, in equilibrium

$$p_E(\mu_1 \otimes \mu_2) = \frac{1}{\Omega(E)} \cdot \begin{cases} 1 & \text{for } \mathcal{H}_1(\mu_1) + \mathcal{H}_2(\mu_2) = E \\ \\ 0 & \text{otherwise} \end{cases} . \tag{IV.3}$$

Since only the overall energy is fixed, the total allowed phase space is computed from

$$\Omega(E) = \int dE_1 \Omega_1(E_1)\Omega_2(E - E_1) = \int dE_1 \exp\left[\frac{S_1(E_1) + S_2(E - E_1)}{k_B}\right]. \tag{IV.4}$$

The properties of the two systems in the new joint equilibrium state are implicit in eq.(IV.3). We can make them explicit by examining the entropy that follows from eq.(IV.4). Extensivity of entropies suggests that S_1 and S_2, are proportional to the number of particles in the systems, making the integrand in eq.(IV.4) an exponentially large quantity. Hence the integral can be equated by the saddle point method to the maximum value of the integrand, obtained for energies E_1^* and $E_2^* = E - E_1^*$, i.e.

$$S(E) = k_B \ln \Omega(E) \approx S_1(E_1^*) + S_2(E_2^*). \tag{IV.5}$$

The position of the maximum is obtained by extremizing the exponent in eq.(IV.4) with respect to E_1, resulting in the condition,

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{\mathbf{x_1}} = \left.\frac{\partial S_2}{\partial E_2}\right|_{\mathbf{x_2}} . \tag{IV.6}$$

Although all joint micro-states are equally likely, the above results indicate that there are an exponentially larger number of states in the vicinity of (E_1^*, E_2^*). Originally, the joint system starts in the vicinity of the point (E_1, E_2). After the exchange of energy takes place, the combined system explores a whole set of new micro-states. The probabilistic arguments provide no information on the dynamics of evolution amongst these micro-states, or on the amount of time needed to establish equilibrium. However, once sufficient

time has elapsed so that the assumption of equal a priori probabilities is again valid, the system is overwhelmingly likely to be at a state with internal energies (E_1^*, E_2^*). At this *equilibrium* point, condition (IV.6) is satisfied, specifying a relation between two functions of state. These state functions are thus equivalent to empirical temperatures, and indeed, consistent with the fundamental result of thermodynamics, we have

$$\left.\frac{\partial S}{\partial E}\right|_{\mathbf{x}} = \frac{1}{T}. \tag{IV.7}$$

• *The first law:* We next inquire about the variations of $S(E, \mathbf{x})$ with $\mathbf{x}$, by changing the coordinates by $\delta\mathbf{x}$. This results in doing work on the system by an amount $đW = \mathbf{J} \cdot \delta\mathbf{x}$, and changes the internal energy to $E + \mathbf{J} \cdot \delta\mathbf{x}$. The first order change in entropy is given by

$$\delta S = S(E + \mathbf{J} \cdot \delta\mathbf{x}, \mathbf{x} + \delta\mathbf{x}) - S(E, \mathbf{x}) = \left(\left.\frac{\partial S}{\partial E}\right|_{\mathbf{x}} \mathbf{J} + \left.\frac{\partial S}{\partial \mathbf{x}}\right|_{E} \right) \cdot \delta\mathbf{x} \quad . \tag{IV.8}$$

This change will occur spontaneously, taking the system into a more probable state, unless the quantity in brackets in zero. Using eq.(IV.7), this allows us to identify the derivatives

$$\left.\frac{\partial S}{\partial x_i}\right|_{E, x_{j\neq i}} = -\frac{J_i}{T}. \tag{IV.9}$$

Having thus identified all variations of S, we have

$$dS(E, \mathbf{x}) = \frac{dE}{T} - \frac{\mathbf{J} \cdot d\mathbf{x}}{T}, \quad \Longrightarrow \quad dE = TdS + \mathbf{J} \cdot d\mathbf{x}, \tag{IV.10}$$

allowing us to identify the heat input $đQ = TdS$.

• *The second law:* Clearly, the above statistical definition of equilibrium rests on the presence of many degrees of freedom $N \gg 1$, which make it exponentially unlikely in N, that the combined systems is found with component energies different from (E_1^*, E_2^*). By this construction, the equilibrium point has a larger number of accessible states than the starting point, i.e.

$$\Omega_1(E_1^*, \mathbf{x}_1)\Omega_2(E_2^*, \mathbf{x}_2) \geq \Omega_1(E_1, \mathbf{x}_1)\Omega_2(E_2, \mathbf{x}_2). \tag{IV.11}$$

In the process of evolving to the more likely (and more densely populated) regions, there is an irreversible loss of information, accompanied by an increase in entropy,

$$\delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geq 0, \tag{IV.12}$$

as required by the second law of thermodynamics. When the two bodies are first brought into contact, the equality in eq.(IV.6) does not hold. The change in entropy is such that

$$\delta S = \left(\left. \frac{\partial S_1}{\partial E_1} \right|_{\mathbf{x_1}} - \left. \frac{\partial S_2}{\partial E_2} \right|_{\mathbf{x_2}} \right) \delta E_1 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_1 \geq 0, \tag{IV.13}$$

i.e. heat (energy) flows from the hotter to the colder body, as in Clausius's statement of the second law.

• *Stability conditions:* Since the point (E_1^*, E_2^*) is a maximum, the second derivative of $S_1(E_1) + S_2(E_2)$ must be negative at this point, i.e.

$$\left. \frac{\partial^2 S_1}{\partial E_1^2} \right|_{\mathbf{x}_1} + \left. \frac{\partial^2 S_2}{\partial E_2^2} \right|_{\mathbf{x}_2} \leq 0. \tag{IV.14}$$

Applying the above condition to two parts of the same system, the condition of thermal stability, $C_{\mathbf{x}} \geq 0$, as discussed in section (I.I), is regained. Similarly, the second order changes in eq.(IV.8) must be negative, requiring that the matrtix $\partial^2 S / \partial x_i \partial x_j \big|_E$ be positive definite.

IV.C Two–Level Systems

Consider N impurity atoms trapped in a solid matrix. Each impurity can be in one of two states, with energies 0 and ϵ respectively. This example is somewhat different from the situations considered so far, in that the allowed micro-states are discrete. Liouville's theorem applies to Hamiltonian evolution in a continuous phase space. Although, there is less ambiguity in enumeration of discrete states, the dynamics that ensures that all allowed micro-states are equally accessed will remain unspecified for the moment. (An example from quantum mechanical evolution will be presented later on.)

The micro-states of the two level system are specified by the set of *occupation numbers* $\{n_i\}$, where $n_i = 0$ or 1 depending on whether the i^{th} impurity is in its ground state or excited. The overall energy is

$$\mathcal{H}\left(\{n_i\}\right) = \epsilon \sum_{i=1}^{N} n_i \equiv \epsilon N_1, \tag{IV.15}$$

where N_1 is the total number of excited impurities. The macro-state is specified by the total energy E, and the number of impurities N. The microcanonical probability is thus

$$p\left(\{n_i\}\right) = \frac{1}{\Omega(E,N)} \delta_{\epsilon \sum_i n_i, E} \quad . \tag{IV.16}$$

As there are $N_1 = E/\epsilon$ excited impurities, the normalization Ω is the number of ways of choosing N_1 excited levels among the available N, and given by the binomial coefficient

$$\Omega(E,N) = \frac{N!}{N_1!\,(N-N_1)!}\,. \tag{IV.17}$$

The entropy

$$S(E,N) = k_B \ln \frac{N!}{N_1!\,(N-N_1)!}\,, \tag{IV.18}$$

can be simplified by Stirling's formula in the limit of $N_1, N \gg 1$ to

$$\begin{aligned} S(E,N) &\approx -Nk_B \left[\frac{N_1}{N}\ln\frac{N_1}{N} + \frac{N-N_1}{N}\ln\frac{N-N_1}{N}\right] \\ &= -Nk_B \left[\left(\frac{E}{N\epsilon}\right)\ln\left(\frac{E}{N\epsilon}\right) + \left(1-\frac{E}{N\epsilon}\right)\ln\left(1-\frac{E}{N\epsilon}\right)\right]. \end{aligned} \tag{IV.19}$$

The equilibrium temperature can now be calculated from eq.(IV.7) as

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = -\frac{k_B}{\epsilon}\ln\left(\frac{E}{N\epsilon - E}\right). \tag{IV.20}$$

Alternatively, the internal energy at a temperature T, is given by

$$E(T) = \frac{N\epsilon}{\exp\left(\frac{\epsilon}{k_B T}\right)+1}\,. \tag{IV.21}$$

The internal energy is a monotonic function of temperature, increasing from a minimum value of 0 at $T = 0$ to a maximum value of $N\epsilon/2$ at infinite temperature. It is, however, possible to start with energies larger than $N\epsilon/2$, which correspond to *negative temperatures* from eq.(IV.20). The origin of the negative temperature is the *decrease* in the number of microstates with increasing energy, the opposite of what happens in most systems. Two level systems have an upper bound on their energy, and very few microstates close to this maximal energy. Hence increased energy leads to more order in the system. However, once a negative temperature system is brought into contact with the rest of the universe (or any portion of it without an upper bound in energy), it loses its excess energy and comes to equilibrium at a positive temperature. The world of negative temperatures is quite unusual in that systems can be cooled by adding heat, and heated by removing it. There are physical examples of systems temporarily prepared at a metastable equilibrium of negative temperature in lasers, and for magnetic spins.

The heat capacity of the system, given by

$$C = \frac{dE}{dT} = Nk_B \left(\frac{\epsilon}{k_B T}\right)^2 \exp\left(\frac{\epsilon}{k_B T}\right) \left(\exp\left(\frac{\epsilon}{k_B T}\right) + 1\right)^{-2}, \tag{IV.22}$$

vanishes at both low and high temperatures. The vanishing of C as $\exp(-\epsilon/k_B T)$ at low temperatures is characteristic of all systems with an *energy gap* separating the ground state and lowest excited states. The vanishing of C at high temperatures is a *saturation* effect, common to systems with a maximum in the number of states as a function of energy. In between, the heat capacity exhibits a peak at a characteristic temperature of $T_\epsilon \propto \epsilon/k_B$.

Statistical mechanics provides much more than just macroscopic quantities such as energy and heat capacity. Eq.(IV.16) is a complete joint probability distribution with considerable information on the micro-states. For example, the unconditional probability for exciting a particular impurity is obtained from

$$p(n_1) = \sum_{\{n_2,\cdots,n_N\}} p(\{n_i\}) = \frac{\Omega(E - n_1\epsilon\,, N-1)}{\Omega(E,N)}. \tag{IV.23}$$

The second equality is obtained by noting that once the energy taken by the first impurity is specified, the remaining energy must be distributed among the other $N-1$ impurities. Using eq.(IV.17),

$$p(n_1 = 0) = \frac{\Omega(E, N-1)}{\Omega(E,N)} = \frac{(N-1)!}{N_1!\,(N-N_1-1)!} \cdot \frac{N_1!\,(N-N_1)!}{N!} = 1 - \frac{N_1}{N}\,, \tag{IV.24}$$

and $p(n_1 = 1) = 1 - p(n_1 = 0) = N_1/N$. Using $N_1 = E/\epsilon$, and eq.(IV.21), the occupation probabilities at a temperature T are

$$p(0) = \frac{1}{1 + \exp\left(-\frac{\epsilon}{k_B T}\right)}, \quad \text{and} \quad p(1) = \frac{\exp\left(-\frac{\epsilon}{k_B T}\right)}{1 + \exp\left(-\frac{\epsilon}{k_B T}\right)}. \tag{IV.25}$$

IV.D The Ideal Gas

As discussed in chapter II, micro-states of a gas of N particles correspond to points $\mu \equiv \{\vec{p}_i, \vec{q}_i\}$, in the $6N$-dimensional phase space. Ignoring the potential energy of interactions, the particles are subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{\vec{p}_i{}^2}{2m} + U(\vec{q}_i) \right], \tag{IV.26}$$

where $U(\vec{q})$ describes the potential imposed by a box of volume V. A microcanonical ensemble is specified by its energy, volume, and number of particles, $M \equiv (E, V, N)$. The joint PDF for a micro-state is

$$p(\mu) = \frac{1}{\Omega(E,V,N)} \cdot \begin{cases} 1 & \text{for } \vec{q}_i \in \text{box, and } \sum_i \vec{p}_i{}^2/2m = E \quad (\pm\Delta_E) \\ 0 & \text{otherwise} \end{cases}. \tag{IV.27}$$

In the allowed micro-states, coordinates of the particles must be within the box, while the momenta are constrained to the surface of the (hyper-)sphere $\sum_{i=1}^{N} \vec{p}_i{}^2 = 2mE$. The allowed phase space is thus the product of a contribution V^N from the coordinates, with the surface area of a $3N$-dimensional sphere of radius $\sqrt{2mE}$ from the momenta. (If the microstate energies are accepted in the energy interval $E \pm \Delta_E$, the corresponding volume in momentum space is that of a (hyper-)spherical shell of thickness $\Delta_R = \sqrt{2m/E}\Delta E$.) The area of a d-dimensional sphere is $\mathcal{A}_d = S_d R^{d-1}$, where S_d is the generalized solid angle.

A simple way to calculate the d–dimensional solid angle is to consider the product of d Gaussian integrals,

$$I_d \equiv \left(\int_{-\infty}^{\infty} dx e^{-x^2} \right)^d = \pi^{d/2}. \tag{IV.28}$$

Alternatively, we may consider I_d as an integral over an entire d–dimensional space, i.e.

$$I_d = \int \prod_{i=1}^{d} dx_i \exp\left(-x_i^2\right). \tag{IV.29}$$

The integrand is spherically symmetric, and we can change coordinates to $R^2 = \sum_i x_i^2$. Noting that the corresponding volume element in these coordinates is $dV_d = S_d R^{d-1} dR$,

$$I_d = \int_0^{\infty} dR S_d R^{d-1} e^{-R^2} = \frac{S_d}{2} \int_0^{\infty} dy y^{d/2-1} e^{-y} = \frac{S_d}{2} (d/2-1)!, \tag{IV.30}$$

where we have first made a change of variables to $y = R^2$, and then used the integral representation of $n!$. Equating expressions (IV.28) and (IV.30) for I_d gives the final result for the solid angle,

$$S_d = \frac{2\pi^{d/2}}{(d/2-1)!}\,. \tag{IV.31}$$

The volume of the available phase space is thus given by

$$\Omega(E,V,N) = V^N \frac{2\pi^{3N/2}}{(3N/2-1)!}(2mE)^{(3N-1)/2}\Delta_R. \tag{IV.32}$$

The entropy is obtained from the logarithm of the above expression. Using Stirling's formula, and neglecting terms of order of 1 or $\ln E \sim \ln N$ in the large N limit, results in

$$\begin{aligned} S(E,V,N) =& k_B\left[N\ln V + \frac{3N}{2}\ln(2\pi mE) - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2}\right] \\ =& Nk_B \ln\left[V\left(\frac{4\pi emE}{3N}\right)^{3/2}\right]. \end{aligned} \tag{IV.33}$$

Properties of the ideal gas can now be recovered from $TdS = dE + PdV - \mu dN$,

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{3}{2}\frac{Nk_B}{E}. \tag{IV.34}$$

The internal energy $E = 3Nk_BT/2$, is only a function of T, and the heat capacity $C_V = 3Nk_B/2$, is a constant. The equation of state is obtained from

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{N,E} = \frac{Nk_B}{V}, \quad \Longrightarrow \quad PV = Nk_BT. \tag{IV.35}$$

The unconditional probability of finding a particle of momentum $\vec{p}_1$ in the gas can be calculated from the joint PDF in eq.(IV.27), by integrating over all other variables,

$$\begin{aligned} p(\vec{p}_1) =& \int d^3\vec{q}_1 \prod_{i=2}^{N} d^3\vec{q}_i d^3\vec{p}_i\, p(\{\vec{q}_i,\vec{p}_i\}) \\ =& \frac{V\,\Omega(E-\vec{p}_1{}^2/2m,\,V,\,N-1)}{\Omega(E,V,N)}\,. \end{aligned} \tag{IV.36}$$

The final expression indicates that once the kinetic energy of one particle is specified, the remaining energy must be shared amongst the other $N-1$. Using eq.(IV.32),

$$\begin{aligned} p(\vec{p}_1) =& \frac{V^N\pi^{3(N-1)/2}(2mE-\vec{p}_1{}^2)^{(3N-4)/2}}{\big(3(N-1)/2-1\big)!}\cdot\frac{(3N/2-1)!}{V^N\pi^{3N/2}(2mE)^{(3N-1)/2}} \\ =& \left(1-\frac{\vec{p}_1{}^2}{2mE}\right)^{3N/2-2}\frac{1}{(2\pi mE)^{3/2}}\frac{(3N/2-1)!}{\big(3(N-1)/2-1\big)!}\,. \end{aligned} \tag{IV.37}$$

From Stirling's formula, the ratio of $(3N/2-1)!$ to $\big(3(N-1)/2-1\big)!$ is approximately $(3N/2)^{3/2}$, and in the large E limit,

$$p(\vec{p}_1) = \left(\frac{3N}{4\pi mE}\right)^{3/2} \exp\left(-\frac{3N}{2}\,\frac{\vec{p}_1{}^{\,2}}{2mE}\right). \tag{IV.38}$$

This is a properly normalized Maxwell-Boltzmann distribution, which can be displayed in its more familiar form after the substitution $E = 3Nk_BT/2$,

$$p(\vec{p}_1) = \frac{1}{(2\pi mk_BT)^{3/2}} \exp\left(-\frac{\vec{p}_1{}^{\,2}}{2mk_BT}\right). \tag{IV.39}$$

IV.E Mixing Entropy and Gibbs' Paradox

The expression in eq.(IV.33) for the entropy of the ideal gas has a major shortcoming in that *it is not extensive*. Under the transformation $(E,V,N) \to (\lambda E, \lambda V, \lambda N)$, the entropy changes to $\lambda(S + Nk_B \ln\lambda)$. The additional term comes from the contribution V^N, of the coordinates to the available phase space. This difficulty is intimately related to the *mixing entropy* of two gases. Consider two distinct gases, initially occupying volumes V_1 and V_2 at the same temperature T. The partition between them is removed, and they are allowed to expand and occupy the combined volume $V = V_1 + V_2$. The mixing process is clearly irreversible, and must be accompanied by an increase in entropy, calculated as follows. According to eq.(IV.33), the initial entropy is

$$S_i = S_1 + S_2 = N_1k_B(\ln V_1 + \sigma_1) + N_2k_B(\ln V_2 + \sigma_2), \tag{IV.40}$$

where,

$$\sigma_\alpha = \ln\left(\frac{4\pi em_\alpha}{3}\cdot\frac{E_\alpha}{N_\alpha}\right)^{3/2}, \tag{IV.41}$$

is the momentum contribution to the entropy of the $\alpha^{\rm th}$ gas. Since $E_\alpha/N_\alpha = 3k_BT/2$ for a monotonic gas,

$$\sigma_\alpha(T) = \frac{3}{2}\ln\left(2\pi em_\alpha k_BT\right). \tag{IV.42}$$

The temperature of the gas is unchanged by mixing, since

$$\frac{3}{2}k_BT_f = \frac{E_1+E_2}{N_1+N_2} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2}k_BT. \tag{IV.43}$$

The final entropy of the mixed gas is

$$S_f = N_1 k_B \ln(V_1 + V_2) + N_2 k_B \ln(V_1 + V_2) + k_B(N_1\sigma_1 + N_2\sigma_2). \tag{IV.44}$$

There is no change in the contribution from the momenta which depends only on temperature. The mixing entropy,

$$\Delta S_{\rm Mix} = S_f - S_i = N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2} = -N k_B \left[\frac{N_1}{N} \ln \frac{V_1}{V} + \frac{N_2}{N} \ln \frac{V_2}{V} \right], \tag{IV.45}$$

is solely from the contribution of the coordinates. The above expression is easily generalized to the mixing of many components, with $\Delta S_{\rm Mix} = -N k_B \sum_\alpha (N_\alpha/N) \ln(V_\alpha/V)$.

Gibbs' Paradox is related to what happens when the two gases, initially on the two sides of the partition, are identical with the same density, $n = N_1/V_1 = N_2/V_2$. Since removing or inserting the partition does not change the state of the system, there should be no entropy of mixing, while eq.(IV.45) does predict such a change. For the resolution of this paradox, note that while after removing and reinserting the partition, the system does return to its initial configuration, the actual particles that occupy the two components are not the same. But as the particles are by assumption *identical*, these configurations cannot be distinguished. In other words, while the exchange of *distinct* particles leads to two configurations

$$\begin{array}{c|c} \bullet & \circ \\ A & B \end{array} \quad \text{and} \quad \begin{array}{c|c} \circ & \bullet \\ A & B \end{array},$$

a similar exchange has no effect on *identical* particles, as in

$$\begin{array}{c|c} \bullet & \bullet \\ A & B \end{array} \quad \text{and} \quad \begin{array}{c|c} \bullet & \bullet \\ A & B \end{array}.$$

Therefore, we have over-counted the phase space associated with N identical particles by the number of possible permutations. As there are $N!$ permutations leading to indistinguishable micro-states, eq.(IV.32) should be corrected to

$$\Omega(N, E, V) = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{(3N/2-1)!} (2mE)^{(3N-1)/2} \Delta_R, \tag{IV.46}$$

resulting in a modified entropy,

$$S = k_B \ln \Omega = k_B[N \ln V - N \ln N + N \ln e] + N k_B \sigma = N k_B \left[\ln \frac{eV}{N} + \sigma \right]. \tag{IV.47}$$

As the argument of the logarithm has changed from V to V/N, the final expression is now properly extensive. The mixing entropies can be recalculated using eq.(IV.47). For the mixing of distinct gases,

$$\begin{aligned}\Delta S_{\rm Mix} = S_f - S_i &= N_1 k_B \ln \frac{V}{N_1} + N_2 k_B \ln \frac{V}{N_2} - N_1 k_B \ln \frac{V_1}{N_1} - N_2 k_B \ln \frac{V_2}{N_2} \\ &= N_1 k_B \ln \left(\frac{V}{N_1} \cdot \frac{N_1}{V_1} \right) + N_2 k_B \ln \left(\frac{V}{N_2} \cdot \frac{N_2}{V_2} \right) \\ &= -N k_B \left[\frac{N_1}{N} \ln \frac{V_1}{V} + \frac{N_2}{N} \ln \frac{V_2}{V} \right],\end{aligned} \tag{IV.48}$$

exactly as obtained before in eq.(IV.45). For the 'mixing' of two identical gases, with $N_1/V_1 = N_2/V_2 = (N_1 + N_2)/(V_1 + V_2)$,

$$\Delta S_{\rm Mix} = S_f - S_i = (N_1 + N_2) k_B \ln \frac{V_1 + V_2}{N_1 + N_2} - N_1 k_B \ln \frac{V_1}{N_1} - N_2 k_B \ln \frac{V_2}{N_2} = 0. \tag{IV.49}$$

Note that after taking the permutations of identical particles into account, the available volume in the final state is $V^{N_1+N_2}/N_1!N_2!$ for distinct particles, and $V^{N_1+N_2}/(N_1+N_2)!$ for identical particles.

- Additional comments on the microcanonical entropy:

1. In the example of two-level impurities in a solid matrix (sec.IV.C), there is no need for the additional factor of $N!$, as the defects can be distinguished by their locations.

2. The corrected formula for the ideal gas entropy in eq.(IV.47) does not affect the computations of energy and pressure in eqs.(IV.34) and (IV.35). It is essential to obtaining an intensive chemical potential,

$$\frac{\mu}{T} = -\left. \frac{\partial S}{\partial N} \right|_{E,V} = -\frac{S}{N} + \frac{5}{2} k_B = k_B \ln \left[\frac{V}{N} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] \quad . \tag{IV.50}$$

3. The above treatment of identical particles is somewhat artificial. This is because the concept of identical particles does not easily fit within the framework of classical mechanics. To implement the Hamiltonian equations of motion on a computer, one has to keep track of the coordinates of the N particles. The computer will have no difficulty in distinguishing exchanged particles. The indistinguishability of their phase spaces is in a sense an additional postulate of classical statistical mechanics. This problem is elegantly resolved within the framework of quantum statistical mechanics. Description of identical particles in quantum mechanics requires proper symmetrization of the wave function. The

corresponding quantum microstates naturally yield the $N!$ factor, as will be shown later on.

4. Yet another difficulty with the expression (IV.47), resolved in quantum statistical mechanics, is the arbitrary constant that appears in changing the units of measurement for q and p. The volume of phase space involves products pq, of coordinates and conjugate momenta, and hence has dimensions of (action)^N. Quantum mechanics provides the appropriate measure of action in Planck's constant h. Anticipating these quantum results, we shall henceforth set the measure of phase space for identical particles to

$$d\Gamma_N = \frac{1}{h^{3N} N!} \prod_{i=1}^{N} d^3\vec{q}_i d^3\vec{p}_i \,. \tag{IV.51}$$

IV.F The Canonical Ensemble

In the microcanonical ensemble, the energy E, of a large macroscopic system is precisely specified, and its equilibrium temperature T, emerges as a consequence (eq.(IV.7)). However, from a thermodynamic perspective, E and T are both functions of state and on the same footing. It is possible to construct a statistical mechanical formulation in which the temperature of the system is specified and its internal energy is then deduced. This is achieved in the *canonical ensemble* where the macro-states, specified by $M \equiv (T, \mathbf{x})$, allow the input of heat into the system, but no external work. The system S, is maintained at a constant temperature through contact with a reservoir R. The *reservoir* is another macroscopic system that is sufficiently large so that its temperature is not changed due to interactions with S. To find the probabilities $p_{(T,\mathbf{x})}(\mu)$, of the various micro-states of S, note that the combined system $R \oplus S$, belongs to a microcanonical ensemble of energy $E_{\rm Tot} \gg E_S$. As in eq.(IV.3), the joint probability of micro-states $(\mu_S \otimes \mu_R)$ is

$$p(\mu_{\rm S} \otimes \mu_{\rm R}) = \frac{1}{\Omega_{\rm S\oplus R}(E_{\rm Tot})} \cdot \begin{cases} 1 & \text{for } \mathcal{H}_{\rm S}(\mu_{\rm S}) + \mathcal{H}_{\rm R}(\mu_{\rm R}) = E_{\rm Tot} \\ 0 & \text{otherwise} \end{cases} . \tag{IV.52}$$

The unconditional probability for micro-states of S is now obtained from

$$p(\mu_{\rm S}) = \sum_{\{\mu_{\rm R}\}} p(\mu_{\rm S} \otimes \mu_{\rm R}) \,. \tag{IV.53}$$

Once $\mu_{\rm S}$ is specified, the above sum is restricted to micro-states of the reservoir with energy $E_{\rm Tot} - \mathcal{H}_{\rm S}(\mu_{\rm S})$. The number of the such states is related to the entropy of the reservoir, and leads to

$$p(\mu_{\rm S}) = \frac{\Omega_{\rm R}\big(E_{\rm Tot} - \mathcal{H}_{\rm S}(\mu_{\rm S})\big)}{\Omega_{\rm S\oplus R}(E_{\rm Tot})} \propto \exp\left[\frac{1}{k_B} S_{\rm R}\big(E_{\rm Tot} - \mathcal{H}_{\rm S}(\mu_{\rm S})\big)\right]. \tag{IV.54}$$

Since by assumption the energy of the system is insignificant compared to that of the reservoir,

$$S_{\rm R}\big(E_{\rm Tot} - \mathcal{H}_{\rm S}(\mu_{\rm S})\big) \approx S_{\rm R}(E_{\rm Tot}) - \mathcal{H}_{\rm S}(\mu_{\rm S})\,\frac{\partial S_{\rm R}}{\partial E_{\rm R}} = S_{\rm R}(E_{\rm Tot}) - \frac{\mathcal{H}_{\rm S}(\mu_{\rm S})}{T}\,. \tag{IV.55}$$

Dropping the subscript S, the normalized probabilities are given by

$$p_{(T,\mathbf{x})}(\mu) = \frac{e^{-\beta\mathcal{H}(\mu)}}{Z(T,\mathbf{x})}. \tag{IV.56}$$

The normalization,

$$Z(T,\mathbf{x}) = \sum_{\{\mu\}} e^{-\beta\mathcal{H}(\mu)}, \tag{IV.57}$$

is known as the *partition function*, and $\beta \equiv 1/k_B T$. (Note that probabilities similar to eq.(IV.56) were already obtained in eqs.(IV.25), and (IV.39), when considering a portion of the system in equilibrium with the rest of it.)

Is the internal energy E, of the system S well defined? Unlike in a microcanonical ensemble, the energy of a system exchanging heat with a reservoir is a random variable. Its probability distribution $p(\mathcal{E})$, is obtained by changing variables from μ to $\mathcal{H}(\mu)$ in $p(\mu)$, resulting in

$$p(\mathcal{E}) = \sum_{\{\mu\}} p\,(\mu)\,\delta\left(\mathcal{H}(\mu) - \mathcal{E}\right) = \frac{e^{-\beta\mathcal{E}}}{Z} \sum_{\{\mu\}} \delta\left(\mathcal{H}(\mu) - \mathcal{E}\right)\,. \tag{IV.58}$$

Since the restricted sum is just the number $\Omega(\mathcal{E})$, of micro-states of appropriate energy,

$$p(\mathcal{E}) = \frac{\Omega(\mathcal{E})e^{-\beta\mathcal{E}}}{Z} = \frac{1}{Z}\exp\left[\frac{S(\mathcal{E})}{k_B} - \frac{\mathcal{E}}{k_B T}\right] = \frac{1}{Z}\exp\left[-\frac{F(\mathcal{E})}{k_B T}\right]\,, \tag{IV.59}$$

where we have set $F = \mathcal{E} - TS(\mathcal{E})$, in anticipation of its relation to the *Helmholtz free energy*. The probability $p(\mathcal{E})$, is sharply peaked at a *most probable energy* E^*, which minimizes $F(\mathcal{E})$. Using the result in sec.(II.F) for sums over exponentials,

$$Z = \sum_{\{\mu\}} e^{-\beta\mathcal{H}(\mu)} = \sum_{\mathcal{E}} e^{-\beta F(\mathcal{E})} \approx e^{-\beta F(E^*)}\,. \tag{IV.60}$$

The *average* energy computed from the distribution in eq.(IV.59) is

$$\langle \mathcal{H} \rangle = \sum_{\mu} \mathcal{H}(\mu) \frac{e^{-\beta \mathcal{H}(\mu)}}{Z} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{\mu} e^{-\beta \mathcal{H}} = -\frac{\partial \ln Z}{\partial \beta} \,. \tag{IV.61}$$

In thermodynamics, a similar expression was encountered for the energy (eq.(I.37)),

$$E = F + TS = F - T \left. \frac{\partial F}{\partial T} \right|_{\mathbf{x}} = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) = \frac{\partial (\beta F)}{\partial \beta}. \tag{IV.62}$$

Eqs.(IV.60) and (IV.61), both suggest identifying

$$F(T, \mathbf{x}) = -k_B T \ln Z(T, \mathbf{x}) \,. \tag{IV.63}$$

However, note that eq.(IV.60) refers to the most likely energy, while the average energy appears in eq.(IV.61). How close are these two values of the energy? We can get an idea of the width of the probability distribution $p(\mathcal{E})$, by computing the variance $\langle \mathcal{H}^2 \rangle_c$. This is most easily accomplished by noting that $Z(\beta)$ is proportional to the characteristic function for $\mathcal{H}$ (with β replacing ik) and,

$$-\frac{\partial Z}{\partial \beta} = \sum_{\mu} \mathcal{H} e^{-\beta \mathcal{H}}, \quad \text{and} \quad \frac{\partial^2 Z}{\partial \beta^2} = \sum_{\mu} \mathcal{H}^2 e^{-\beta \mathcal{H}}. \tag{IV.64}$$

Cumulants of $\mathcal{H}$ are generated by $\ln Z(\beta)$,

$$\langle \mathcal{H} \rangle_c = \frac{1}{Z} \sum_{\mu} \mathcal{H} e^{-\beta \mathcal{H}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}, \tag{IV.65}$$

and

$$\langle \mathcal{H}^2 \rangle_c = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{1}{Z} \sum_{\mu} \mathcal{H}^2 e^{-\beta \mathcal{H}} - \frac{1}{Z^2} \left(\sum_{\mu} \mathcal{H} e^{-\beta \mathcal{H}} \right)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta}. \tag{IV.66}$$

More generally, the n^{th} cumulant of $\mathcal{H}$ is given by

$$\langle \mathcal{H}^n \rangle_c = (-1)^n \frac{\partial^n \ln Z}{\partial \beta^n}. \tag{IV.67}$$

From eq.(IV.66),

$$\langle \mathcal{H}^2 \rangle_c = -\frac{\partial \langle \mathcal{H} \rangle}{\partial (1/k_B T)} = k_B T^2 \left. \frac{\partial \langle \mathcal{H} \rangle}{\partial T} \right|_{\mathbf{x}}, \quad \Rightarrow \quad \langle \mathcal{H}^2 \rangle_c = k_B T^2 C_{\mathbf{x}}, \tag{IV.68}$$

where we have identified the heat capacity with the thermal derivative of the average energy $\langle \mathcal{H} \rangle$. Eq.(IV.68) shows that it is justified to treat the mean and most likely energies interchangeably, since the width of the distribution $p(\mathcal{E})$, only grows as $\sqrt{\langle \mathcal{H}^2 \rangle_c} \propto N^{1/2}$. The relative error, $\sqrt{\langle \mathcal{H}^2 \rangle_c}/\langle \mathcal{H} \rangle_c$ vanishes in the thermodynamic limit as $1/\sqrt{N}$. (In fact eq.(IV.67) shows that all cumulants of $\mathcal{H}$ are proportional to N.) The PDF for energy in a canonical ensemble can thus be approximated by

$$p(\mathcal{E}) = \frac{1}{Z} e^{-\beta F(\mathcal{E})} \approx \exp\left(-\frac{(\mathcal{E} - \langle \mathcal{H} \rangle)^2}{2 k_B T^2 C_{\mathbf{x}}} \right) \frac{1}{\sqrt{2\pi k_B T^2 C_{\mathbf{x}}}}. \tag{IV.69}$$

The above distribution is sufficiently sharp to make the internal energy in a canonical ensemble unambiguous in the $N \to \infty$ limit. Some care is necessary if the heat capacity $C_{\mathbf{x}}$ is divergent, as is the case in some continuous phase transitions.

The canonical probabilities in eq.(IV.56) are unbiased estimates obtained (as in sec.(II.G)) by constraining the *average energy*. The entropy of the canonical ensemble can also be calculated directly from eq.(IV.56) (using eq.(III.68)) as

$$S = -k_B \langle \ln p(\mu) \rangle = -k_B \langle (-\beta \mathcal{H} - \ln Z) \rangle = \frac{E - F}{T}, \tag{IV.70}$$

again using the identification of $\ln Z$ with the free energy from eq.(IV.63). For any finite system, the canonical and microcanonical probabilities are distinct. However, in the so called *thermodynamic limit* of $N \to \infty$ limit, the canonical probabilities are so sharply peaked around the average energy that they are essentially indistinct from microcanonical probabilities at that energy. The following table compares the prescriptions used in the two ensembles.

Ensemble	Macro-state	$p(\mu)$	Normalization
Microcanonical	$(E, \mathbf{x})$	$\delta_\Delta\big(\mathcal{H}(\mu) - E\big)/\Omega$	$S(E, \mathbf{x}) \quad = \quad k_B \ln \Omega$
Canonical	$(T, \mathbf{x})$	$\exp\big(-\beta \mathcal{H}(\mu)\big)/Z$	$F(T, \mathbf{x}) = -k_B T \ln Z$

Table 3: Comparison of canonical and microcanonical ensembles.

IV.G Examples

The two examples of sections (IV.C) and (IV.D) are now reexamined in the canonical ensemble.

1. *Two level systems:* The N impurities are described by a macro-state $M \equiv (T, N)$. Subject to the Hamiltonian $\mathcal{H} = \epsilon \sum_{i=1}^{N} n_i$, the canonical probabilities of the micro-states $\mu \equiv \{n_i\}$, are given by

$$p\left(\{n_i\}\right) = \frac{1}{Z} \exp\left[-\beta\epsilon \sum_{i=1}^{N} n_i\right]. \tag{IV.71}$$

From the partition function,

$$\begin{aligned} Z(T,N) &= \sum_{\{n_i\}} \exp\left[-\beta\epsilon \sum_{i=1}^{N} n_i\right] = \left(\sum_{n_1=0}^{1} e^{-\beta\epsilon n_1}\right) \cdots \left(\sum_{n_N=0}^{1} e^{-\beta\epsilon n_N}\right) \\ &= \left(1 + e^{-\beta\epsilon}\right)^N, \end{aligned} \tag{IV.72}$$

we obtain the free energy

$$F(T,N) = -k_B T \ln Z = -N k_B T \ln\left[1 + e^{-\epsilon/(k_B T)}\right]. \tag{IV.73}$$

The entropy is now given by

$$S = -\left.\frac{\partial F}{\partial T}\right|_N = \underbrace{N k_B \ln\left[1 + e^{-\epsilon/(k_B T)}\right]}_{-F/T} + N k_B T \left(\frac{\epsilon}{k_B T^2}\right) \frac{e^{-\epsilon/(k_B T)}}{1 + e^{-\epsilon/(k_B T)}}. \tag{IV.74}$$

The internal energy,

$$E = F + TS = \frac{N\epsilon}{1 + e^{\epsilon/(k_B T)}}, \tag{IV.75}$$

can also be obtained from

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{N\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}. \tag{IV.76}$$

Since the joint probability in eq.(IV.71) is in the form of a product, the excitations of different impurities are *independent* of each other, with the unconditional distribution

$$p(n) = \frac{e^{-\beta\epsilon n}}{1 + e^{-\beta\epsilon}}. \tag{IV.77}$$

This result coincides with eqs.(IV.25), obtained through a more elaborate analysis in the microcanonical ensemble. As expected, in the large N limit, the canonical and microcanonical ensembles describe exactly the same physics, both at the macroscopic and microscopic levels.

2. *The Ideal Gas:* For the canonical macro-state $M \equiv (T, V, N)$, the joint PDF for the micro-states $\mu \equiv \{\vec{p}_i, \vec{q}_i\}$, is

$$p(\{\vec{p}_i, \vec{q}_i\}) = \frac{1}{Z} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] \cdot \begin{cases} 1 & \text{for } \{\vec{q}_i\} \in \text{box} \\ \\ 0 & \text{otherwise} \end{cases} . \tag{IV.78}$$

Including the modifications to the phase space of identical particles in eq.(IV.51), the dimensionless partition function is computed as

$$\begin{aligned} Z(T, V, N) = & \int \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3\vec{q}_i d^3\vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] \\ = & \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda(T)^3}\right)^N , \end{aligned} \tag{IV.79}$$

where

$$\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}} , \tag{IV.80}$$

is a characteristic length associated with the action h. It shall be demonstrated later on that this length scale controls the onset of quantum mechanical effects in an ideal gas.

The free energy is given by

$$\begin{aligned} F = -k_B T \ln Z &= -N k_B T \ln V + N k_B T \ln N - N k_B T - \frac{3N}{2} k_B T \ln\left(\frac{2\pi m k_B T}{h^2}\right) \\ &= -N k_B T \left[\ln\left(\frac{Ve}{N}\right) + \frac{3}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] . \end{aligned} \tag{IV.81}$$

Various thermodynamic properties of the ideal gas can now be obtained from $dF = -SdT - PdV + \mu dN$. For example, from the entropy

$$-S = \left.\frac{\partial F}{\partial T}\right|_{V,N} = -N k_B \left[\ln\frac{Ve}{N} + \frac{3}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] - N k_B T \frac{3}{2T} = \frac{F - E}{T}, \tag{IV.82}$$

we obtain the internal energy $E = 3N k_B T/2$. The equation of state is obtained from

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{N k_B T}{V}, \qquad \Longrightarrow \quad PV = N k_B T, \tag{IV.83}$$

and the chemical potential is given by

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = \frac{F}{N} + k_B T = \frac{E - TS + PV}{N} = k_B T \ln\left(n\lambda^3\right) . \tag{IV.84}$$

Also, according to eq.(IV.78), the momenta of the N particles are taken from independent Maxwell–Boltzmann distributions, consistent with eq.(IV.39).

IV.H The Gibbs Canonical Ensemble

We can also define a generalized canonical ensemble in which the internal energy changes by the addition of both heat and work. The macrostates $M \equiv (T, \mathbf{J})$, are specified in terms of the external temperature and forces acting on the system; the thermodynamic coordinates $\mathbf{x}$ appear as additional random variables. The system is maintained at constant force through external elements (e.g. pistons or magnets). Including the work done against the forces, the energy of the combined system that includes these elements is $\mathcal{H} - \mathbf{J} \cdot \mathbf{x}$. Note that while the work done *on the system* is $+\mathbf{J} \cdot \mathbf{x}$, the energy change associated with the external elements with coordinates $\mathbf{x}$ has the opposite sign. The microstates of this combined system occur with the (canonical) probabilities

$$p(\mu_{\rm S}, \mathbf{x}) = \exp\left[-\beta \mathcal{H}(\mu_{\rm S}) + \beta \mathbf{J} \cdot \mathbf{x}\right] / \mathcal{Z}(T, N, \mathbf{J}) \,, \tag{IV.85}$$

with the *Gibbs partition function*,

$$\mathcal{Z}(N, T, \mathbf{J}) = \sum_{\mu_{\rm S}, \mathbf{x}} e^{\beta \mathbf{J} \cdot \mathbf{x} - \beta \mathcal{H}(\mu_{\rm S})} \,. \tag{IV.86}$$

(Note that we have explicitly included the particle number N to indicate that there is no chemical work. Chemical work is considered in the Grand Canonical Ensemble, which is discussed next.)

In this ensemble, the expectation value of the coordinates is obtained from

$$\langle \mathbf{x} \rangle = k_B T \frac{\partial \ln \mathcal{Z}}{\partial \mathbf{J}}, \tag{IV.87}$$

which together with the thermodynamic identity $\mathbf{x} = -\partial G / \partial \mathbf{J}$, suggests the identification

$$G(N, T, \mathbf{J}) = -k_B T \ln \mathcal{Z}, \tag{IV.88}$$

where $G = E - TS - \mathbf{x} \cdot \mathbf{J}$ is the *Gibbs free energy*. (The same conclusion can be reached by equating $\mathcal{Z}$ in eq.(IV.86) to the term that maximizes the probability with respect to $\mathbf{x}$.) The *enthalpy* $H \equiv E - \mathbf{x} \cdot \mathbf{J}$ is easily obtained in this ensemble from

$$-\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \langle \mathcal{H} - \mathbf{x} \cdot \mathbf{J} \rangle = H. \tag{IV.89}$$

Note that heat capacities at constant force (which include work done against the external forces), are obtained from the enthalpy as $C_{\mathbf{J}} = \partial H / \partial T$.

The following examples illustrate the use of the Gibbs canonical ensemble:

1. *The Ideal Gas* in the *isobaric* ensemble is described by the macrostate $M \equiv (N, T, P)$. A micro-state $\mu \equiv \{\vec{p}_i, \vec{q}_i\}$, with a volume V occurs with the probability

$$p(\{\vec{p}_i, \vec{q}_i\}, V) = \frac{1}{\mathcal{Z}} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta PV\right] \cdot \begin{cases} 1 & \text{for } \{\vec{q}_i\} \in \text{box of volume } V \\ 0 & \text{otherwise} \end{cases} . \quad \text{(IV.90)}$$

The normalization factor is now

$$\begin{aligned} \mathcal{Z}(N, T, P) &= \int_0^\infty dV e^{-\beta PV} \int \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3\vec{q}_i d^3\vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] \\ &= \int_0^\infty dV V^N e^{-\beta PV} \frac{1}{N! \lambda(T)^{3N}} = \frac{1}{\left(\beta P \lambda(T)^3\right)^N}. \end{aligned} \quad \text{(IV.91)}$$

The Gibbs free energy is given by

$$G = -k_B T \ln \mathcal{Z} = N k_B T \left[\ln P - \frac{5}{2} \ln\left(k_B T\right) + \frac{3}{2} \ln\left(\frac{h^2}{2\pi m}\right)\right]. \quad \text{(IV.92)}$$

Starting from $dG = -SdT + VdP + \mu dN$, the volume of the gas is obtained as

$$V = \left.\frac{\partial G}{\partial P}\right|_{T,N} = \frac{N k_B T}{P}, \qquad \Longrightarrow \quad PV = N k_B T. \quad \text{(IV.93)}$$

The *enthalpy* $H = \langle E + PV \rangle$ is easily calculated from

$$H = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{5}{2} N k_B T,$$

from which we get $C_P = dH/dT = 5/2 N k_B$.

2. *Spins* in an external magnetic field $\vec{B}$, provide a common example for usage of the Gibbs canonical ensemble. Adding the work done against the magnetic field to the internal Hamiltonian $\mathcal{H}$, results in the Gibbs partition function

$$\mathcal{Z}(N, T, B) = \text{tr}\left[\exp\left(-\beta \mathcal{H} + \beta \vec{B} \cdot \vec{M}\right)\right],$$

where $\vec{M}$ is the net *magnetization*. The symbol tr is used to indicate the sum over all spin degrees of freedom, which in a quantum mechanical formulation are restricted to discrete values. The simplest case is spin of 1/2, with two possible projections of the spin along the magnetic field. A microstate of N spins is now described by the set of *Ising* variables $\{\sigma_i = \pm 1\}$. The corresponding magnetization along the field direction is given

by $M = \mu_0 \sum_{i=1}^{N} \sigma_i$, where μ_0 is a microscopic magnetic moment. Assuming that there are no interactions between spins ($\mathcal{H} = 0$), the probability of a microstate is

$$p\left(\{\sigma_i\}\right) = \frac{1}{\mathcal{Z}} \exp\left[\beta B \mu_0 \sum_{i=1}^{N} \sigma_i\right]. \tag{IV.94}$$

Clearly, this is closely related to the example of two level systems discussed in the canonical ensemble, and we can easily obtain the Gibbs partition function

$$\mathcal{Z}(N, T, B) = \left[2\cosh(\beta\mu_0 B)\right]^N, \tag{IV.95}$$

and the Gibbs free energy

$$G = -k_B T \ln \mathcal{Z} = -N k_B T \ln\left[2\cosh(\beta\mu_0 B)\right]. \tag{IV.96}$$

The average magnetization is given by

$$M = -\frac{\partial G}{\partial B} = N\mu_0 \tanh(\beta\mu_0 B). \tag{IV.97}$$

Expanding eq.(IV.97) for small B results in the well-known Curie law for magnetic *susceptibility* of non-interacting spins,

$$\chi(T) = \left.\frac{\partial M}{\partial B}\right|_{B=0} = \frac{N\mu_0^2}{k_B T}. \tag{IV.98}$$

The enthalpy is simply $H = \langle \mathcal{H} - BM \rangle = -BM$, and $C_B = -B\partial M/\partial T$.

IV.I The Grand Canonical Ensemble

The previous sections demonstrate that while the canonical and microcanonical ensembles are completely equivalent in the thermodynamic limit, it is frequently much easier to perform statistical mechanical computations in the canonical framework. Sometimes it is more convenient to allow chemical work (by fixing the chemical potential μ, rather than at a fixed number of particles), but no mechanical work. The resulting macro-states $M \equiv (T, \mu, \mathbf{x})$, are governed by the *grand canonical* ensemble. The corresponding micro-states $\mu_{\rm S}$, contain an indefinite number of particles $N(\mu_{\rm S})$. As in the case of the canonical ensemble, the system S, can be maintained at a constant chemical potential through contact

with a reservoir R, at temperature T and chemical potential μ. The probability distribution for the micro-states of S is obtained by summing over all states of the reservoir, as in eq.(IV.53), and is given by

$$p(\mu_{\rm S}) = \exp\left[\beta\mu N(\mu_{\rm S}) - \beta\mathcal{H}(\mu_{\rm S})\right]/\mathcal{Q}\,. \tag{IV.99}$$

The normalization factor is the *grand partition function*,

$$\mathcal{Q}(T,\mu,\mathbf{x}) = \sum_{\mu_{\rm S}} e^{\beta\mu N(\mu_{\rm S})-\beta\mathcal{H}(\mu_{\rm S})}\,. \tag{IV.100}$$

We can reorganize the above summation by grouping together all micro-states with a given number of particles, i.e.

$$\mathcal{Q}(T,\mu,\mathbf{x}) = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{(\,\mu_{\rm S}|N)} e^{-\beta\mathcal{H}_N(\mu_{\rm S})}\,. \tag{IV.101}$$

The restricted sums in eq.(IV.101) are just the N-particle partition functions. As each term in $\mathcal{Q}$ is the total weight of all micro-states of N particles, the unconditional probability of finding N particles in the system is

$$p(N) = \frac{e^{\beta\mu N} Z(T,N,\mathbf{x})}{\mathcal{Q}(T,\mu,\mathbf{x})}. \tag{IV.102}$$

The average number of particles in the system is

$$\langle N\rangle = \frac{1}{\mathcal{Q}}\frac{\partial}{\partial(\beta\mu)}\mathcal{Q} = \frac{\partial}{\partial(\beta\mu)}\ln\mathcal{Q}, \tag{IV.103}$$

while the number fluctuations are related to the variance

$$\langle N^2\rangle_C = \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\mathcal{Q}}\frac{\partial^2}{\partial(\beta\mu)^2}\ln\mathcal{Q} - \left(\frac{\partial}{\partial(\beta\mu)}\ln\mathcal{Q}\right)^2 = \frac{\partial^2}{\partial(\beta\mu)^2}\ln\mathcal{Q} = \frac{\partial\,\langle N\rangle}{\partial(\beta\mu)}. \tag{IV.104}$$

The variance is thus proportional to N, and the *relative number fluctuations* vanish in the thermodynamic limit, establishing the equivalence of this ensemble to the previous ones.

Because of the sharpness of the distribution for N, the sum in eq.(IV.101) can be approximated by its largest term at $N = N^* \approx < N >$, i.e.

$$\begin{aligned}\mathcal{Q}(T,\mu,\mathbf{x}) &= \lim_{N\to\infty}\sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,N,\mathbf{x}) = e^{\beta\mu N^*} Z(T,N^*,\mathbf{x}) = e^{\beta\mu N^* - \beta F} \\ &= e^{-\beta(-\mu N^* + E - TS)} = e^{-\beta\mathcal{G}},\end{aligned} \tag{IV.105}$$

where

$$\mathcal{G}(T,\mu,\mathbf{x}) = E - TS - \mu N = -k_B T \ln \mathcal{Q}, \tag{IV.106}$$

is the *grand potential*. Thermodynamic information is obtained by using $d\mathcal{G} = -SdT - Nd\mu + \mathbf{J}\cdot d\mathbf{x}$, as

$$-S = \left.\frac{\partial \mathcal{G}}{\partial T}\right|_{\mu,\mathbf{x}}, \qquad N = -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{T,\mathbf{x}}, \qquad J_i = \left.\frac{\partial \mathcal{G}}{\partial x_i}\right|_{T,\mu}. \tag{IV.107}$$

As a final example, we compute the properties of the ideal gas of non-interacting particles in the grand canonical ensemble. The macro-state is $M \equiv (T,\mu,V)$, and the corresponding micro-states $\{\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,\cdots\}$ have indefinite particle number. The grand partition function is given by

$$\begin{aligned}
\mathcal{Q}(T,\mu,V) &= \sum_{N=0}^{\infty} e^{\beta\mu N}\frac{1}{N!}\int\left(\prod_{i=1}^{N}\frac{d^3\vec{q}_i d^3\vec{p}_i}{h^3}\right)\exp\left[-\beta\sum_i \frac{p_i^2}{2m}\right] \\
&= \sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{N!}\left(\frac{V}{\lambda^3}\right)^N \qquad (\text{with } \lambda = \frac{h}{\sqrt{2\pi m k_B T}}) \\
&= \exp\left[e^{\beta\mu}\frac{V}{\lambda^3}\right],
\end{aligned} \tag{IV.108}$$

and the grand potential is

$$\mathcal{G}(T,\mu,V) = -k_B T \ln \mathcal{Q} = -k_B T e^{\beta\mu}\frac{V}{\lambda^3}\,. \tag{IV.109}$$

But, since $\mathcal{G} = E - TS - \mu N = -PV$, the gas pressure can be obtained directly as

$$P = -\frac{\mathcal{G}}{V} = -\left.\frac{\partial \mathcal{G}}{\partial V}\right|_{\mu,T} = k_B T\frac{e^{\beta\mu}}{\lambda^3}. \tag{IV.110}$$

The particle number and the chemical potential are related by

$$N = -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{T,V} = \frac{e^{\beta\mu}V}{\lambda^3}. \tag{IV.111}$$

The equation of state is obtained by comparing eqs.(IV.110) and (IV.111), as $P = k_B T N/V$. Finally, the chemical potential is given by

$$\mu = k_B T \ln\left(\lambda^3\frac{N}{V}\right) = k_B T \ln\left(\frac{P\lambda^3}{k_B T}\right). \tag{IV.112}$$

V. Interacting Particles

V.A The Cumulant Expansion

The examples studied in the previous section involve non-interacting particles. It is precisely the lack of interactions that renders these problems exactly solvable. Interactions, however, are responsible for the wealth of interesting materials and phases observed in nature. We would thus like to understand the role of interactions amongst particles, and learn how to treat them in statistical mechanics. For a general Hamiltonian,

$$\mathcal{H}_N = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \mathcal{U}(\vec{q}_1, \cdots, \vec{q}_N), \tag{V.1}$$

the partition function can be written as

$$\begin{aligned} Z(T,V,N) =& \frac{1}{N!} \int \prod_{i=1}^{N} \left(\frac{d^3\vec{p}_i d^3\vec{q}_i}{h^3} \right) \exp\left[-\beta \sum_i \frac{\vec{p}_i^{\,2}}{2m} \right] \exp\left[-\beta \mathcal{U}(\vec{q}_1, \cdots, \vec{q}_N) \right] \\ =& Z_0(T,V,N) \left\langle \exp\left[-\beta \mathcal{U}(\vec{q}_1, \cdots, \vec{q}_N) \right] \right\rangle^0 , \end{aligned} \tag{V.2}$$

where $Z_0(T,V,N) = \left(V/\lambda^3\right)^N / N!$ is the partition function of the *ideal gas* (eq.(IV.73)), and $\langle \mathcal{O} \rangle^0$ denotes the expectation value of $\mathcal{O}$ computed with the probability distribution of the non-interacting system. In terms of the cumulants of the random variable $\mathcal{U}$, eq.(V.2) can be recast as

$$\ln Z = \ln Z_0 + \sum_{\ell=1}^{\infty} \frac{(-\beta)^\ell}{\ell!} \left\langle \mathcal{U}^\ell \right\rangle_c^0 . \tag{V.3}$$

The cumulants are related to the moments by the relations in section II.B. Since $\mathcal{U}$ depends only on $\{\vec{q}_i\}$ which are uniformly *and independently* distributed within the box of volume V, the moments are given by

$$\left\langle \mathcal{U}^\ell \right\rangle^0 = \int \left(\prod_{i=1}^{N} \frac{d^3\vec{q}_i}{V} \right) \mathcal{U}(\vec{q}_1, \cdots, \vec{q}_N)^\ell . \tag{V.4}$$

Various expectation values can also be calculated perturbatively, from

$$\begin{aligned} \langle \mathcal{O} \rangle =& \frac{1}{Z} \frac{1}{N!} \int \prod_{i=1}^{N} \left(\frac{d^3\vec{p}_i d^3\vec{q}_i}{h^3} \right) \exp\left[-\beta \sum_i \frac{\vec{p}_i^{\,2}}{2m} \right] \exp\left[-\beta \mathcal{U}(\vec{q}_1, \cdots, \vec{q}_N) \right] \times \mathcal{O} \\ =& \frac{\langle \mathcal{O} \exp\left[-\beta \mathcal{U} \right] \rangle^0}{\langle \exp\left[-\beta \mathcal{U} \right] \rangle^0} = i \, \frac{\partial}{\partial k} \ln \langle \exp\left[-ik\mathcal{O} - \beta \mathcal{U} \right] \rangle^0 \Big|_{k=0} . \end{aligned} \tag{V.5}$$

The final expectation value generates the joint cumulants of the random variables $\mathcal{O}$ and $\mathcal{U}$, as

$$\ln \langle \exp\left[-ik\mathcal{O} - \beta\mathcal{U}\right]\rangle^0 \equiv \sum_{\ell,\ell'=1}^{\infty} \frac{(-ik)^{\ell'}}{\ell'!}\frac{(-\beta)^{\ell}}{\ell!}\left\langle \mathcal{O}^{\ell'}\mathcal{U}^{\ell}\right\rangle_c^0 , \tag{V.6}$$

resulting in

$$\langle \mathcal{O}\rangle = \sum_{\ell=0}^{\infty} \frac{(-\beta)^{\ell}}{\ell!}\left\langle \mathcal{O}\mathcal{U}^{\ell}\right\rangle_c^0 . \tag{V.7}$$

The simplest system for treating interactions is again the dilute gas. As discussed in chapter II, for a weakly interacting gas we can specialize to

$$\mathcal{U}(\vec{q}_1,\cdots,\vec{q}_N) = \sum_{i<j}\mathcal{V}(\vec{q}_i - \vec{q}_j)\,, \tag{V.8}$$

where $\mathcal{V}(\vec{q}_i - \vec{q}_j)$ is a pair-wise interaction between particles. The first correction in eq.(V.3) is

$$\begin{aligned}\langle \mathcal{U}\rangle_c^0 =& \sum_{i<j}\int \frac{d^3\vec{q}_i}{V}\frac{d^3\vec{q}_j}{V}\mathcal{V}(\vec{q}_i - \vec{q}_j) \\ =& \frac{N(N-1)}{2V}\int d^3\vec{q}\,\mathcal{V}(\vec{q})\,.\end{aligned} \tag{V.9}$$

The final result is obtained by performing the integrals over the relative and center of mass coordinates of $\vec{q}_i$ and $\vec{q}_j$ separately. (Each of the $N(N-1)/2$ pairs makes an identical contribution.)

The second order correction,

$$\left\langle \mathcal{U}^2\right\rangle_c^0 = \sum_{i<j,\,k<l}\left[\langle \mathcal{V}(\vec{q}_i - \vec{q}_j)\mathcal{V}(\vec{q}_k - \vec{q}_l)\rangle^0 - \langle \mathcal{V}(\vec{q}_i - \vec{q}_j)\rangle^0\langle \mathcal{V}(\vec{q}_k - \vec{q}_l)\rangle^0\right], \tag{V.10}$$

is the sum of $[N(N-1)/2]^2$ terms that can be grouped as follows:

(i) There is no contribution from terms in which the four indices $\{i,j,k,l\}$ are different. This is because the different $\{\vec{q}_i\}$ are independently distributed and $\langle \mathcal{V}(\vec{q}_i - \vec{q}_j)\mathcal{V}(\vec{q}_k - \vec{q}_l)\rangle^0$ equals $\langle \mathcal{V}(\vec{q}_i - \vec{q}_j)\rangle^0\langle \mathcal{V}(\vec{q}_k - \vec{q}_l)\rangle^0$.

(ii) There is one common index between the two pairs, e.g. $\{(i,j),(i,l)\}$. By changing coordinates to $\vec{q}_{ij} = \vec{q}_i - \vec{q}_j$ and $\vec{q}_{il} = \vec{q}_i - \vec{q}_l$, it again follows that $\langle \mathcal{V}(\vec{q}_i - \vec{q}_j)\mathcal{V}(\vec{q}_i - \vec{q}_l)\rangle^0$ equals $\langle \mathcal{V}(\vec{q}_i - \vec{q}_j)\rangle^0\langle \mathcal{V}(\vec{q}_i - \vec{q}_l)\rangle^0$. The vanishing of these terms is a consequence of the *translational symmetry* of the problem in the absence of an external potential.

(iii) In the remaining $N(N-1)/2$ terms the pairs are identical, resulting in

$$\left\langle \mathcal{U}^2 \right\rangle_c^0 = \frac{N(N-1)}{2} \left[\int \frac{d^3\vec{q}}{V} \mathcal{V}(\vec{q})^2 - \left(\int \frac{d^3\vec{q}}{V} \mathcal{V}(\vec{q}) \right)^2 \right] . \tag{V.11}$$

The second term in the above equation is smaller by a factor of d^3/V, where d is a characteristic range for the potential $\mathcal{V}$. For any reasonable potential that decays with distance, this term vanishes in the thermodynamic limit.

Similar groupings occur for higher order terms in this *cumulant expansion*. It is helpful to visualize the terms in the expansion diagrammatically as follows:

(a) For a term of order ℓ, draw ℓ pairs of points (representing $\vec{q}_i$ and $\vec{q}_j$) connected by bonds, representing the interaction $\mathcal{V}_{ij} \equiv \mathcal{V}(\vec{q}_i - \vec{q}_j)$. An overall factor of $1/\ell!$ accompanies such graphs.

(b) By multiple selections of the same index i, two or more bonds can be joined together forming a diagram of interconnected points. There is a factor S_ℓ associated with the number of ways of assigning labels 1 through N to the different points of the graph. Ignoring the differences between N, $N-1$, etc., a diagram with n_s points makes a contribution proportional to N^{n_s}. There is typically also division by a *symmetry factor* which takes into account the number of equivalent assignments. For example, the diagrams involving a pair of points, calculated in eqs.(V.9) and (V.11), have a symmetry factor of 1/2.

(c) Apart from these numerical prefactors, the contribution of a diagram is an integral R_ℓ over all the n_s coordinates $\vec{q}_i$, of products of corresponding $\mathcal{V}_{ij}$. If the graphs has n_c *disconnected clusters*, integration over the center of mass coordinates of the clusters gives a factor of V^{n_c}.

Fortunately, many cancellations occur in calculating cumulants. In particular:

• When calculating the moment $\left\langle U^\ell \right\rangle^0$, the contribution of a *disconnected diagram* is simply the product of its *disjoint clusters*. The coordinates of these clusters are independent random variables, and make no contribution to the joint cumulant $\left\langle U^\ell \right\rangle_c^0$. This result also ensures the extensivity of $\ln Z$, as the surviving connected diagrams give a factor of V from their center of mass integration. (Disconnected clusters have more factors of V, and are non-extensive.)

• There are also *one particle reducible* clusters which are fully connected, yet fall to disjoint fragments if a *single* coordinate point is removed. By measuring all other coordinates relative to this special point, it can be seen that (in a translationally invariant system)

the value of such a diagram is the product of its disjoint fragments. It can be shown that such diagrams are also cancelled out in calculating the cumulant. Thus only *one particle irreducible* clusters survive in this cumulant expansion. A cluster with n_s sites and ℓ bonds makes a contribution of order of $N(N/V)^{n_s-1}(\beta\mathcal{V})^\ell$ to $\ln Z$.

Ignoring terms of order of $1/N$, the cumulant expansion leads to a corrected free energy,

$$F(T,V,N) = F_0(T,V,N) + \frac{N^2}{2V}\left(\int d^3\vec{q}\,\mathcal{V}(\vec{q}) - \frac{\beta}{2}\int d^3\vec{q}\mathcal{V}(\vec{q})^2 + \mathcal{O}\left(\beta^2\mathcal{V}^3\right)\right) + \mathcal{O}\left(\frac{N^3\beta^2\mathcal{V}^3}{V^2}\right). \tag{V.12}$$

From this expression we can proceed to calculate other modified state functions, e.g. $P = -\,\partial F/\partial V|_{T,N}$. Unfortunately, the expansion in powers of $\beta\mathcal{V}$ is not particularly useful. The inter-atomic potential $\mathcal{V}(\vec{r})$ for most particles has an attractive tail due to van der Waals interactions that decays as $-1/r^6$ at large separations $r = |\vec{r}|$. At short distances the overlap of the electron clouds makes the potential strongly repulsive. Typically there is a minimum of depth a few hundred degrees Kelvin, at a distance of a few angstroms. The infinity in $\mathcal{V}(\vec{r})$ at short distances makes it an unsuitable expansion parameter. This problem can be alleviated by a partial resummation of diagrams. For example, to get the correction at order of N^2/V, we need to sum over all two point clusters, independent of the number of bonds. The resulting sum is actually quite trivial, and leads to

$$\begin{aligned}\ln Z &= \ln Z_0 + \sum_{n=1}^{\infty}\frac{(-\beta)^n}{n!}\frac{N(N-1)}{2}\int\frac{d^3\vec{q}}{V}\mathcal{V}(\vec{q})^n + \mathcal{O}\left(\frac{N^3}{V^2}\right)\\ &= \ln Z_0 + \frac{N(N-1)}{2V}\int d^3\vec{q}\,[\exp\left(-\beta\mathcal{V}(\vec{q})\right) - 1] + \mathcal{O}\left(\frac{N^3}{V^2}\right).\end{aligned} \tag{V.13}$$

The quantity $f(\vec{q}) = \exp\left(-\beta\mathcal{V}(\vec{q})\right) - 1$ is a much more convenient expansion parameter which goes to -1 at short distances and rapidly vanishes for large separations. In the next section we shall recast the perturbative expansion in terms of this quantity.

V.B The Cluster Expansion

For short range interactions, specially with a hard core, it is much better to replace the expansion parameter $\mathcal{V}(\vec{q})$ by $f(\vec{q}) = \exp\left(-\beta\mathcal{V}(\vec{q})\right) - 1$, which is obtained by summing over all possible number of bonds between two points on a cumulant graph. The resulting series is organized in powers of the density N/V, and is most suitable for obtaining a *virial expansion*, which expresses the deviations from the ideal gas equation of state in a power series

$$\frac{P}{k_B T} = \frac{N}{V}\left[1 + B_2(T)\frac{N}{V} + B_3(T)\left(\frac{N}{V}\right)^2 + \cdots\right]. \tag{V.14}$$

The temperature dependent parameters, $B_i(T)$, are known as the *virial coefficients* and originate from the inter-particle interactions. Our initial goal is to compute these coefficients from first principles.

To illustrate a different method of expansion, we shall perform computations in the grand canonical ensemble. With a macro-state $M \equiv (T, \mu, V)$, the grand partition function is given by

$$\mathcal{Q}(\mu, T, V) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N, T, V) = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^N \mathcal{S}_N, \tag{V.15}$$

where

$$\mathcal{S}_N = \int \prod_{i=1}^{N} d^3\vec{q}_i \prod_{i<j} (1 + f_{ij}), \tag{V.16}$$

and $f_{ij} = f(\vec{q}_i - \vec{q}_j)$.

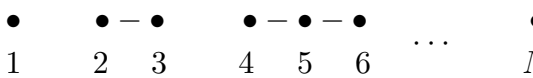
The $2^{N(N-1)/2}$ terms in $\mathcal{S}_N$ can now be ordered in powers of f_{ij} as

$$\mathcal{S}_N = \int \prod_{i=1}^{N} d^3\vec{q}_i \left(1 + \sum_{i<j} f_{ij} + \sum_{i<j,k<l} f_{ij} f_{kl} + \cdots\right). \tag{V.17}$$

An efficient method for organizing the perturbation series is to represent the various contributions diagrammatically. In particular we shall apply the following conventions:

(a) Draw N dots labelled by $i = 1, \cdots, N$ to represent the coordinates $\vec{q}_1$ through $\vec{q}_N$,

(b) Each term in eq.(V.17) corresponds to a product of f_{ij}, represented by drawing lines connecting i and j for each f_{ij}. For example, the graph,



represents the integral

$$\left(\int d^3\vec{q}_1\right)\left(\int d^3\vec{q}_2 d^3\vec{q}_3 f_{23}\right)\left(\int d^3\vec{q}_4 d^3\vec{q}_5 d^3\vec{q}_6 f_{45} f_{56}\right)\cdots\left(\int d^3\vec{q}_N\right)\ .$$

As the above example indicates, the value of each graph is the product of the contributions from its *linked clusters*. Since these clusters are more fundamental, we reformulate the sum in terms of them by defining a quantity b_ℓ, equal to the *sum over all ℓ-particle linked clusters* (one-particle irreducible or not). For example

$$b_1 = \quad \bullet \quad = \int d^3\vec{q} = V, \tag{V.18}$$

and

$$b_2 = \bullet - \bullet = \int d^3\vec{q}_1 d^3\vec{q}_2 f(\vec{q}_1 - \vec{q}_2). \tag{V.19}$$

There are four diagrams contributing to b_3, leading to

$$b_3 = \int d^3\vec{q}_1 d^3\vec{q}_2 d^3\vec{q}_3 \big[f(\vec{q}_1-\vec{q}_2)f(\vec{q}_2-\vec{q}_3) + f(\vec{q}_2-\vec{q}_3)f(\vec{q}_3-\vec{q}_1) + f(\vec{q}_3-\vec{q}_1)f(\vec{q}_1-\vec{q}_2) + f(\vec{q}_1-\vec{q}_2)f(\vec{q}_2-\vec{q}_3)f(\vec{q}_3-\vec{q}_1)\big]. \tag{V.20}$$

A given N-particle graph can be decomposed to n_1 1-clusters, n_2 2-clusters, $\cdots$, n_ℓ ℓ-clusters, etc. Hence,

$$\mathcal{S}_N = \sum_{\{n_\ell\}'} \prod_\ell b_\ell^{n_\ell} W(\{n_\ell\}), \tag{V.21}$$

where the restricted sum is over all *distinct divisions of N points* into a set of clusters $\{n_\ell\}$, such that $\sum_\ell \ell n_\ell = N$. The coefficients $W(\{n_\ell\})$ are the number of ways of assigning N particle labels to groups of n_ℓ ℓ-clusters. For example, the divisions of 3 particles into a 1-cluster and a 2-cluster are

$$\underset{1}{\bullet} \quad \underset{2\quad 3}{\bullet-\bullet}\ , \quad \underset{2}{\bullet} \quad \underset{1\quad 3}{\bullet-\bullet}\ , \text{ and } \quad \underset{3}{\bullet} \quad \underset{2\quad 1}{\bullet-\bullet}\ .$$

All above graphs have $n_1 = 1$ and $n_2 = 1$, and contribute a factor of $b_1 b_2$ to S_3; thus $W(1,1) = 3$.

In general, $W(\{n_\ell\})$ is the number of distinct ways of grouping the labels $1,\ldots,N$ into bins of n_ℓ ℓ-clusters. It can be obtained from the total number of permutations, $N!$, after dividing by the number of equivalent assignments. Within each bin of ℓn_ℓ particles, equivalent assignments are obtained by: (i) permuting the ℓ labels in each subgroup in $\ell!$

ways, for a total of $(\ell!)^{n_\ell}$ permutations; and (ii) the $n_\ell!$ rearrangements of the n_ℓ subgroups. Hence,

$$W(\{n_\ell\}) = \frac{N!}{\prod_\ell n_\ell!(\ell!)^{n_\ell}}. \tag{V.22}$$

(We can indeed check that $W(1,1) = 3!/(1!)(2!) = 3$ as obtained above.)

Using the above value of W, the expression for $\mathcal{S}_N$ in eq.(V.21) can be evaluated. However, the restriction of the sum to configurations such that $\sum_\ell \ell n_\ell = N$ complicates the evaluation. Fortunately, this restriction disappears in the expression for the grand partition function in eq.(V.16),

$$\mathcal{Q} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^N \sum_{\{n_\ell\}'} \frac{N!}{\prod_\ell n_\ell!(\ell!)^{n_\ell}} \prod_\ell b_\ell^{n_\ell}. \tag{V.23}$$

The restriction in the second sum is now removed by noting that $\sum_{N=0}^{\infty} \sum_{\{n_\ell\}} \delta_{\sum_\ell \ell n_\ell, N} = \sum_{\{n_\ell\}}$. Therefore,

$$\begin{aligned}
\mathcal{Q} &= \sum_{\{n_\ell\}} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{\sum_\ell \ell n_\ell} \prod_\ell \frac{b_\ell^{n_\ell}}{n_\ell!(\ell!)^{n_\ell}} = \sum_{\{n_\ell\}} \prod_\ell \frac{1}{n_\ell!} \left(\frac{e^{\beta\mu\ell} b_\ell}{\lambda^{3\ell}\ell!}\right)^{n_\ell} \\
&= \prod_\ell \sum_{\{n_\ell\}} \frac{1}{n_\ell!} \left[\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{b_\ell}{\ell!}\right]^{n_\ell} = \prod_\ell \exp\left[\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{b_\ell}{\ell!}\right] \\
&= \exp\left[\sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{b_\ell}{\ell!}\right].
\end{aligned} \tag{V.24}$$

The above result has the simple geometrical interpretation that the sum over all graphs, connected or not, equals the exponential of the sum over *connected* graphs. This is a quite general result that is also related to the graphical connection between moments and cumulants discussed in sec.II.B.

The grand potential is now obtained from

$$\ln \mathcal{Q} = -\beta\mathcal{G} = \frac{PV}{kT} = \sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{b_\ell}{l!}. \tag{V.25}$$

In eq.(V.25), the extensivity condition is used to get $\mathcal{G} = E - TS - \mu N = -PV$. Thus the terms on the right hand side of the above equation must also be proportional to the volume V. This can be explicitly verified by noting that in evaluating each b_ℓ there is an

integral over the center of mass coordinate that explores the whole volume. For example, $b_2 = \int d^3\vec{q}_1 d^3\vec{q}_2 f(\vec{q}_1 - \vec{q}_2) = V \int d^3\vec{q}_{12} f(\vec{q}_{12})$. Quite generally, we can set

$$\lim_{V\to\infty} b_\ell = V\bar{b}_\ell, \tag{V.26}$$

and the pressure is now obtained from

$$\frac{P}{kT} = \sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{\bar{b}_\ell}{\ell!}. \tag{V.27}$$

The linked cluster theorem ensures $\mathcal{G} \propto V$, since if any non-linked cluster had appeared in $\ln \mathcal{Q}$, it would have contributed a higher power of V.

Although an expansion for the gas pressure, eq.(V.27) is quite different from eq.(V.14) in that it involves powers of $e^{\beta\mu}$ rather than the density $n = N/V$. This difference can be removed by solving for the density in terms of the chemical potential, using

$$N = \frac{\partial \ln \mathcal{Q}}{\partial(\beta\mu)} = \sum_{\ell=1}^{\infty} \ell \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{V\bar{b}_\ell}{\ell!}. \tag{V.28}$$

The equation of state can be obtained by eliminating the *fugacity* $x = e^{\beta\mu}/\lambda^3$, between the equations

$$n = \sum_{\ell=1}^{\infty} \frac{x^\ell}{(\ell-1)!}\bar{b}_\ell, \qquad \text{and} \qquad \frac{P}{kT} = \sum_{\ell=1}^{\infty} \frac{x^\ell}{\ell!}\bar{b}_\ell, \tag{V.29}$$

using the following steps:

(a) Solve for $x(n)$ from ($\bar{b}_1 = \int d^3\vec{q}/V = 1$)

$$x = n - \bar{b}_2 x^2 - \frac{\bar{b}_3}{2}x^3 - \cdots. \tag{V.30}$$

The perturbative solution at each order is obtained by substituting the solution at the previous order in eq.(V.30),

$$\begin{aligned} x_1 &= n + \mathcal{O}(n^2) \\ x_2 &= n - \bar{b}_2 n^2 + \mathcal{O}(n^3) \\ x_3 &= n - \bar{b}_2(n - \bar{b}_2 n)^2 - \frac{\bar{b}_3}{2}n^3 + \mathcal{O}(n^4) = n - \bar{b}_2 n^2 + (2\bar{b}_2^2 - \frac{\bar{b}_3}{2})n^3 + \mathcal{O}(n^4). \end{aligned} \tag{V.31}$$

(b) Substitute the perturbative result for $x(n)$ into eq.(V.29), yielding

$$\begin{aligned}\beta P &= x + \frac{b_2}{2}x^2 + \frac{b_3}{6}x^3 + \cdots \\ &= n - b_2 n^2 + (2b_2^2 - \frac{b_3}{2})n^3 + \frac{b_2}{2}n^2 - b_2^2 n^3 + \frac{b_3}{6}n^3 + \cdots \\ &= n - \frac{b_2}{2}n^2 + (b_2^2 - \frac{b_3}{3})n^3 + \mathcal{O}(n^4).\end{aligned} \tag{V.32}$$

The final result is in the form of the virial expansion of eq.(V.14),

$$\beta P = n + \sum_{\ell=2}^{\infty} B_\ell(T) n^\ell.$$

The first term in the series reproduces the ideal gas result. The next two corrections are

$$B_2 = -\frac{b_2}{2} = -\frac{1}{2}\int d^3\vec{q}\,\left(e^{-\beta\mathcal{V}(\vec{q})} - 1\right), \tag{V.33}$$

and

$$\begin{aligned}B_3 &= b_2^2 - \frac{b_3}{3} \\ &= \left(\int d^3\vec{q}\,\left(e^{-\beta\mathcal{V}(\vec{q})} - 1\right)\right)^2 \\ &- \frac{1}{3}\left[3\int d^3\vec{q}_{12}d^3\vec{q}_{13}f(\vec{q}_{12})f(\vec{q}_{13}) + \int d^3\vec{q}_{12}d^3\vec{q}_{13}f(\vec{q}_{12})f(\vec{q}_{13})f(\vec{q}_{12}-\vec{q}_{13})\right] \\ &= -\frac{1}{3}\int d^3\vec{q}_{12}d^3\vec{q}_{13}f(\vec{q}_{12})f(\vec{q}_{13})f(\vec{q}_{12}-\vec{q}_{13}).\end{aligned} \tag{V.34}$$

The above example demonstrates the cancellation of the one particle reducible cluster that appears in b_3. While all clusters (reducible or not) appear in the sum for b_ℓ, as demonstrated in the previous section, only the *one particle irreducible* ones can appear in an expansion in powers of density. The final expression for the $\ell^{\rm th}$ virial coefficient is

$$B_\ell(T) = -\frac{(\ell-1)}{\ell!}\,\bar{d}_\ell, \tag{V.35}$$

where $\bar{d}_\ell$ is defined as the sum over all one–particle–irreducible clusters of ℓ points. Note that in terms of $\bar{d}_\ell$, the partition function can be organized as

$$\ln Z = \ln Z_0 + V\sum_{\ell=2}^{\infty}\frac{n^\ell}{\ell!}\bar{d}_\ell, \tag{V.36}$$

reproducing the above virial expansion from $\beta P = \partial \ln Z/\partial V$.

V.C The Second Virial Coefficient & van der Waals Equation

Let us study the second virial coefficient B_2, for a typical gas using eq.(V.33). As discussed before, the two-body potential is characterized by a hard core repulsion at short distances and a van der Waals attraction at large distances. To make the computations easier, we shall use the following approximation for the potential,

$$\mathcal{V}(r) = \begin{cases} +\infty & \text{for } r < r_0 \\ \\ -u_0 \left(r_0/r\right)^6 & \text{for } r > r_0 \end{cases}, \tag{V.37}$$

which combines both features. The contributions of the two portions can then be calculated separately as,

$$\begin{aligned} b_2 &= \int_0^\infty d^3\vec{r} \left(e^{-\beta \mathcal{V}(r)} - 1 \right) \\ &= \int_0^{r_0} 4\pi r^2 dr (-1) + \int_{r_0}^\infty 4\pi r^2 dr \left[e^{+\beta u_0 (r_0/r)^6} - 1 \right]. \end{aligned} \tag{V.38}$$

The second integrand can be approximated by $\beta u_0 (r_0/r)^6$ in the high temperature limit, $\beta u_0 \gg 1$, and leads to

$$B_2 = -\frac{1}{2} \left[-\frac{4\pi r_0^3}{3} + 4\pi \beta u_0 r_0^6 \left(-\frac{r^{-3}}{3} \right) \Big|_{r_0}^\infty \right] = \frac{2\pi r_0^3}{3} (1 - \beta u_0). \tag{V.39}$$

We can define an *excluded volume* of $\Omega = 4\pi r_0^3/3$ which is 8 times the atomic volume (since the distance of minimum approach r_0, is twice an atomic radius), to get

$$B_2(T) = \frac{\Omega}{2} \left(1 - \frac{u_0}{k_B T} \right). \tag{V.40}$$

- Remarks and observations:

(1) The tail of the van der Waals attractive potential ($\propto r^{-6}$) extends to very long separations. Yet, its integral in eq.(V.39) is dominated by contributions from the short scales r_0. In this limited context, the van der Waals potential is *short-ranged*, and results in corrections to the ideal gas behavior that are *analytical* in density n, leading to the virial series.

(2) By contrast, potentials that fall off with separation as $1/r^3$ or slower, are *long-ranged*. The integral appearing in calculation of the second virial coefficient is dominated by long distances, and is divergent. As a result, corrections to the ideal gas behavior can

not be written in the form of a virial series, and are in fact *non-analytic*. A good example is provided by the Coulomb interactions (see problems for the test), where the non-analytic corrections can be obtained by summing all the *ring diagrams* in the cumulant (or cluster) expansions.

(3) The second virial coefficient has dimensions of volume, and (for short-range potentials) is proportional to the atomic volume Ω. In the high temperature limit, the importance of corrections to ideal gas behavior can be estimated by comparing the first two terms of eq.(V.14),

$$\frac{B_2 n^2}{n} = \frac{B_2}{n^{-1}} \sim \frac{\text{Atomic volume}}{\text{volume per particle in gas}} \sim \frac{\text{gas density}}{\text{liquid density}}. \tag{V.41}$$

This ratio is roughly 10^{-3} for air at room temperature and pressure. The corrections to ideal gas behavior are thus small at low densities. On dimensional grounds, a similar ratio is expected for the higher order terms, $B_\ell n^\ell / B_{\ell-1} n^{\ell-1}$, in the virial series. We may thus suspect the convergence of the series at high enough densities (when the gas liquifies).

(4) The virial expansion breaks down not only at high densities, but also at low temperatures. This is suggested by the divergences in eqs.(V.40) and (V.38) as $T \to 0$, and reflects the fact that in the presence of attractive interactions the particles can lower their energy at low temperatures by condensing into a liquid state.

(5) The truncated virial expansion,

$$\frac{P}{k_B T} = n + \frac{\Omega}{2}\left(1 - \frac{u_0}{k_B T}\right) n^2 + \cdots, \tag{V.42}$$

can be rearranged as

$$\frac{1}{k_B T}\left(P + \frac{u_0 \Omega}{2} n^2\right) = n\left(1 + n\frac{\Omega}{2} + \cdots\right) \approx \frac{n}{1 - n\Omega/2} = \frac{N}{V - N\Omega/2}. \tag{V.43}$$

This is precisely in the form of the *van der Waals* equation

$$\left[P + \frac{u_0 \Omega}{2}\left(\frac{N}{V}\right)^2\right]\left[V - \frac{N\Omega}{2}\right] = N k_B T, \tag{V.44}$$

and we can identify the *van der Waals parameters*, $a = u_0\Omega/2$ and $b = \Omega/2$.

• *Physical interpretation of the van der Waals equation:* Historically, van der Waals suggested eq.(V.44) on the basis of experimental results for the equation of state of various

gases, towards the end of the19th century. At that time the microscopic interactions between gas particles were not known, and van der Waals postulated the necessity of an attractive interaction between gas atoms based on the observed decreases in pressure. It was only later on that such interactions were observed directly, and then attributed to the induced dipole–dipole forces by London. The physical justification of the correction terms is as follows.

(a) There is a correction to the gas volume V due to the hard core exclusions. At first sight, it may appear surprising that the *excluded volume* b, in eq.(V.44) is one half of the volume that is excluded around each particle. This is because this factor measures a *joint* excluded volume involving all particles in phase space. In fact, the contribution of coordinates to the partition function of the hard-core gas can be estimated at *low densities*, from

$$\mathcal{S}_N = \int' \frac{\prod_i d^3\vec{q}_i}{N!} = \frac{1}{N!} V\big(V-\Omega\big)\big(V-2\Omega\big)\cdots\big(V-(N-1)\Omega\big) \approx \frac{1}{N!}\left(V-\frac{N\Omega}{2}\right)^N . \tag{V.45}$$

The above result is obtained by adding particles one at a time, and noting that the available volume for the $m^{\rm th}$ particle is $(V-m\Omega)$. At low densities, the overall effect is a reduction of the volume available to each particle by approximately $\Omega/2$. Of course, the above result is only approximate, since the effects of excluded volume involving more than two particles are not correctly taken into account. The relatively simple form of eq.(V.45) is only exact at for spatial dimensions $d = 1$ and infinity. As proved in problems for the test, the exact excluded volume in $d = 1$ is in fact Ω.

(b) The decrease in pressure P, due to attractive interactions, is somewhat harder to quantify. In sec.III.F, the gas pressure was related to the impacts of particles on a wall via

$$P = \overline{(nv_x)(2mv_x)}\Big|_{v_x<0} = nm\overline{v_x^2}, \tag{V.46}$$

where the first term is the number of collisions per unit time and area, while the second is the momentum imparted by each particle. For the ideal gas, the usual equation of state is recovered by noting that the average kinetic energy is $m\overline{v_x^2}/2 = k_BT/2$. Attractive interactions lead to a reduction in pressure given by

$$\delta P = \delta n\left(m\overline{v_x^2}\right) + n\delta\left(m\overline{v_x^2}\right). \tag{V.47}$$

While different statistical ensembles give the same pressure, which is a bulk state function, they may lead to different behaviors at the surface. We must thus be careful, and consistent, in evaluation of eq.(V.47), which depends of surface properties.

In a canonical ensemble, the gas density is *reduced* at the walls. This is because the particles in the middle of the box experience an attractive potential V from all sides, while at the edge only an attractive energy of $V/2$ is available from half of the space. The resulting change in density is approximately

$$\delta n \approx n\left(e^{-\beta V/2} - e^{-\beta V}\right) \approx \beta n V/2. \tag{V.48}$$

Integrating the interaction of one particle in the bulk with the rest gives

$$V = \int d^3\,\vec{r}\,\mathcal{V}_{\rm attr.}(r)\,n = -n\Omega u_0. \tag{V.49}$$

The change in density thus gives the pressure correction of $\delta P = -n^2\Omega u_0/2$ calculated in eq.(V.44). There is no correction to the kinetic energy of the particles impinging on the wall, since in the canonical formulation the probabilites for momentum and location of the particles are independent variables. The probability distribution for momentum is *uniform* in space, giving the average kinetic energy of $k_B T/2$ for each direction of motion.

A different explanation is presented in a kinetic formulation in which particles follow the deterministic Hamiltonian equations of motion. In this formulation, the impinging particles lose kinetic energy in approaching the wall from the surface, since they have to climb out of the potential well set up by the attractions of bulk particles. The reduction in kinetic energy is given by

$$\delta\frac{m v_x^2}{2} = \frac{1}{2}\int d^3\,\vec{r}\,\mathcal{V}_{\rm attr.}(r)\,n = -\frac{1}{2}n\Omega u_0. \tag{V.50}$$

The reduced velocities lead to an *increase* in the surface density in this case, as the slower particles spend a longer time τ in the vicinity of the wall! The relative change in density is given by

$$\frac{\delta n}{n} = \frac{\delta\tau}{\tau} = -\frac{\delta v_x}{v_x} = -\frac{1}{2}\frac{\delta v_x^2}{v_x^2}, \qquad \Longrightarrow \qquad \delta n = -\beta n V/2. \tag{V.51}$$

The increase in density is precisely the opposite of the result of eq.(V.48) in the canonical formulation. However, with the decrease in kinetic energy calculated in eq.(V.50), it again leads to the correct reduction in pressure.

V.D Breakdown of the van der Waals equation

As discussed in sec.I.I, mechanical stability of a gas requires the positivity of the isothermal compressibility, $\kappa_T = -V^{-1}\,\partial V/\partial P|_T$. This condition can be obtained by examining density fluctuations in a grand canonical ensemble. The probability of finding N particles in a volume V is given by eq.(IV.102) as

$$p(N,V) = \frac{e^{\beta\mu N} Z(T,N,V)}{\mathcal{Q}}. \tag{V.52}$$

Since for a gas $\ln \mathcal{Q} = -\beta\mathcal{G} = PV/k_BT$, eqs.(IV.103) and (IV.104) simplify to

$$\begin{cases} \langle N\rangle_c = N = \dfrac{\partial(\ln \mathcal{Q})}{\partial(\beta\mu)} = V\,\left.\dfrac{\partial P}{\partial \mu}\right|_{T,V}, \\ \langle N^2\rangle_c = \dfrac{\partial^2(\ln \mathcal{Q})}{\partial(\beta\mu)^2} = \dfrac{\partial\langle N\rangle_c}{\partial(\beta\mu)} = k_BT\,\left.\dfrac{\partial N}{\partial \mu}\right|_{T,V}. \end{cases} \tag{V.53}$$

Dividing the two equations, and using the chain rule, results in

$$\frac{\langle N^2\rangle_c}{N} = \frac{k_BT}{V}\,\left.\frac{\partial N}{\partial P}\right|_{T,V} = -\frac{k_BT}{V}\,\left.\frac{\partial N}{\partial V}\right|_{P,T}\,\left.\frac{\partial V}{\partial P}\right|_{N,T} = nk_BT\kappa_T. \tag{V.54}$$

The positivity of κ_T is thus tied to that of the variance of N. A stable value of N corresponds to a *maximum* of the probability $p(N,V)$, i.e. a positive compressibility. A negative κ_T actually corresponds to a *minimum* in $p(N,V)$ implying that the system is least likely to be found at such densities. Fluctuations in density will then occur spontaneously and change the density to a stable value.

Any approximate equation of state, such as the van der Waals equation, must at least satisfy the stability requirements. However, the van der Waals isotherms contain a portion with $-\,\partial P/\partial V|_T < 0$, for temperatures less than a critical value T_c. The negative compressibility implies an instability towards forming domains of lower and higher density, i.e. phase separation. The attractive interactions in real gases do indeed result in a liquid–gas phase separation at low temperatures. The isotherms then include a flat portion, $\partial P/\partial V|_T = 0$, at the coexistence of the two phases. Can the (unstable) van der Waals isotherms be used to construct the phase diagram of a real gas?

One way of doing so is by the following *Maxwell construction*: The variations of the chemical potential $\mu(T,P)$, along an isotherm are obtained by integrating eq.(V.53), as

$$d\mu = \frac{V}{N}dP, \quad \Longrightarrow \quad \mu(T,P) = \mu(T,P_A) + \int_{P_A}^{P} dP'\frac{V(T,P')}{N}. \tag{V.55}$$

Since the van der Waals isotherms for $T < T_c$ are non-monotonic, there is a range of pressures that correspond to three different values, $\{\mu_\alpha\}$, of the chemical potential. The possibility of several values of μ at a given temperature and pressure indicates phase coexistence. In equilibrium, the number of particles in each phase N_α, adjusts so as to minimize the Gibbs free energy $G = \sum_\alpha \mu_\alpha N_\alpha$. Clearly, the phase with lowest μ_α will acquire all the particles. A phase transition occurs when two branches of allowed chemical potentials intersect. From eq.(V.55), the critical pressure P_c, for this intersection is obtained from the condition

$$\oint_{P_c}^{P_c} dP' V(T, P') = 0. \tag{V.56}$$

A geometrical interpretation of the above result is that P_c corresponds to a pressure that encloses equal areas of the non-monotonic isotherm on each side. The Maxwell construction approach to phase condensation is somewhat unsatisfactory, as it relies on integrating a clearly unphysical portion the van der Waals isotherm. A better approach that makes the approximations involved more apparent is presented in the next section.

V.E Mean Field Theory of Condensation

In principle, all properties of the interacting system, including phase separation, are contained within the thermodynamic potentials that can be obtained by evaluating $Z(T, N)$ or $\mathcal{Q}(T, \mu)$. Phase transitions, however, are characterized by discontinuities in various state functions and must correspond to the appearance of singularities in the partition functions. At first glance, it is somewhat surprising that any singular behavior should emerge from computing such well behaved integrals (for short-ranged interactions) as

$$Z(T, N, V) = \int \frac{\prod_{i=1}^{N} d^3\vec{p}_i d^3\vec{q}_i}{N! h^{3N}} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta \sum_{i<j} \mathcal{V}(\vec{q}_i - \vec{q}_j)\right]. \tag{V.57}$$

Instead of evaluating the integrals perturbatively, we shall now set up a reasonable approximation scheme. The contributions of the hard core and attractive portions of the potential are again treated separately, and the partition function approximated by

$$Z(T, N, V) \approx \frac{1}{N!} \frac{1}{\lambda^{3N}} \underbrace{V\big(V - \Omega\big) \cdots \big(V - (N-1)\Omega\big)}_{\text{Excluded volume effects}} \exp(-\beta \bar{U}). \tag{V.58}$$

Here $\bar{U}$ represents an average attraction energy, obtained by assuming a *uniform density* $n = N/V$, as

$$\begin{aligned}\bar{U} =& \frac{1}{2}\sum_{i,j}\mathcal{V}_{\rm attr.}(\vec{q}_i - \vec{q}_j) = \frac{1}{2}\int d^3\vec{r}_1 d^3\vec{r}_2 n(\vec{r}_1) n(\vec{r}_2)\mathcal{V}_{\rm attr.}(\vec{r}_1 - \vec{r}_2) \\ \approx& \frac{n^2}{2} V \int d^3\vec{r}\,\mathcal{V}_{\rm attr.}(\vec{r}) \equiv -\frac{N^2}{2V}\,u.\end{aligned} \tag{V.59}$$

The parameter u describes the net effect of the attractive interactions. Substituting into eq.(V.58) leads to the following approximation for the partition function

$$Z(T,N,V) \approx \frac{(V - N\Omega/2)^N}{N!\lambda^{3N}} \exp\left[\frac{\beta u N^2}{2V}\right]. \tag{V.60}$$

From the resulting free energy,

$$F = -k_B T \ln Z = -N k_B T \ln(V - N\Omega/2) + N k_B T \ln(N/e) + 3N k_B T \ln\lambda - \frac{uN^2}{2V}, \tag{V.61}$$

we obtain the expression for the pressure in the canonical ensemble as

$$P_{\rm can} = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{N k_B T}{V - N\Omega/2} - \frac{uN^2}{2V^2}. \tag{V.62}$$

Remarkably, the uniform density approximation reproduces the van der Waals equation of state. However, the self-consistency of this approximation can now be checked. As long as κ_T is positive, eq.(V.54) implies that the variance of density vanishes for large volumes as $\langle n^2 \rangle_c = k_B T n^2 \kappa_T / V$. But κ_T diverges at T_c, and at lower temperatures its negativity implies an instability towards density fluctuations as discussed in the previous section. When condensation occurs, there is phase separation into high (liquid) and low (gas) density states, and the uniform density assumption becomes manifestly incorrect. This difficulty is circumvented in the *grand canonical ensemble*. Once the chemical potential is fixed, the number of particles (and hence density) in this ensemble is automatically adjusted to that of the appropriate phase.

As the assumption of a uniform density is correct for both the liquid and gas phases, we can use the approximations of eqs.(V.59) and (V.60) to estimate the grand partition function

$$\mathcal{Q}(T,\mu,V) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,N,V) \approx \sum_{N=0}^{\infty} \exp\left[N\ln\left(\frac{V}{N} - \frac{\Omega}{2}\right) + \frac{\beta u N^2}{2V} + \Delta N\right], \tag{V.63}$$

where $\Delta = 1 + \beta\mu - \ln(\lambda^3)$. As in any sum over exponentials in N, the above expression is dominated by a particular value of particle number (hence density), and given by

$$\mathcal{Q}(T,\mu,V) \approx \exp\left\{\max\left[N\Delta + N\ln\left(\frac{V}{N} - \frac{\Omega}{2}\right) + \frac{\beta u N^2}{2V}\right]_N\right\}. \tag{V.64}$$

Hence, the grand canonical expression for the gas pressure is obtained from

$$\beta P_{\rm g.c} = \frac{\ln \mathcal{Q}}{V} = \max[\Psi(n)]_n, \tag{V.65}$$

where

$$\Psi(n) = n\Delta + n\ln\left(n^{-1} - \frac{\Omega}{2}\right) + \frac{\beta u}{2}n^2. \tag{V.66}$$

The possible values of density are obtained from $d\Psi/dn|_{n_\alpha} = 0$, and satisfy

$$\Delta = -\ln\left(n_\alpha^{-1} - \frac{\Omega}{2}\right) + \frac{1}{1 - n_\alpha\Omega/2} - \beta u n_\alpha. \tag{V.67}$$

The above equation in fact admits multiple solutions n_α for the density. Substituting the resulting Δ into eq.(V.65) leads after some manipulation to

$$P_{\rm g.c.} = \max\left[\frac{n_\alpha k_B T}{1 - n_\alpha\Omega/2} - \frac{u}{2}n_\alpha^2\right]_\alpha = \max[P_{\rm can}(n_\alpha)]_\alpha, \tag{V.68}$$

i.e. the grand canonical and canonical values of pressure are identical at a particular density. However, if eq.(V.67) admits multiple solutions for the density at a particular chemical potential, the correct density is uniquely determined as the one that maximizes the canonical expression for pressure (or for $\psi(n)$).

The mechanism for the liquid–gas phase transition is therefore the following. The sum in eq.(V.63) is dominated by two large terms at the liquid and gas densities. At a particular chemical potential, the stable phase is determined by the larger of the two terms. The phase transition occurs when the dominant term changes upon varying the temperature. In mathematical form

$$\ln \mathcal{Q} = \lim_{V\to\infty} \ln\left[e^{\beta V P_{\rm liquid}} + e^{\beta V P_{\rm gas}}\right] = \begin{cases} \beta V P_{\rm gas} & \text{for } T > T^* \\ \beta V P_{\rm liquid} & \text{for } T < T^* \end{cases}. \tag{V.69}$$

The origin of the singularity in density can thus be traced to the thermodynamic limit of $V \to \infty$. There are no phase transitions in finite systems!

V.F Variational Methods

Perturbative methods provide a systematic way of incorporating the effect of interactions, but are impractical for the study of strongly interacting systems. While the first few terms in the virial series slightly modify the behavior of the gas, an infinite number of terms have to be summed to obtain the condensation transition. An alternative, *but approximate*, method for dealing with strongly interacting systems is the use of variational methods.

Suppose that in an appropriate ensemble we need to calculate $Z = \mathrm{tr}\left(e^{-\beta\mathcal{H}}\right)$. In the canonical formulation, Z is the partition function corresponding to the Hamiltonian $\mathcal{H}$ at temperature $k_B T = 1/\beta$, and for a classical system tr refers to the integral over the phase space of N particles. However, the method is more general and can be applied to Gibbs or Grand partition functions with the appropriate modification of the exponential factor; also in the context of quantum systems where tr is a sum over all allowed quantum microstates. Let us assume that calculating Z is very difficult for the (interacting) Hamiltonian $\mathcal{H}$, but that there is another Hamiltonian $\mathcal{H}_0$ *acting on the same set of degrees of freedom* for which the calculations are easier. We then introduce a Hamiltonian $\mathcal{H}(\lambda) = \mathcal{H}_0 + \lambda\,(\mathcal{H} - \mathcal{H}_0)$, and a corresponding partition function

$$Z(\lambda) = \mathrm{tr}\{\exp\left[-\beta\mathcal{H}_0 - \lambda\beta\,(\mathcal{H} - \mathcal{H}_0)\right]\}, \tag{V.70}$$

which interpolates between the two as λ changes from zero to one. It is then easy to prove the convexity condition

$$\frac{d^2 \ln Z(\lambda)}{d\lambda^2} = \beta^2 \left\langle \left(\mathcal{H} - \mathcal{H}_0\right)^2 \right\rangle_c \geq 0, \tag{V.71}$$

where $\langle\rangle$ is an expectation value with the appropriately normalized probability.

From the convexity of the function, it immediately follows that

$$\ln Z(\lambda) \geq \ln Z(0) + \lambda \left.\frac{d \ln Z}{d\lambda}\right|_{\lambda=0}. \tag{V.72}$$

But it is easy to see that $d\ln Z/d\lambda|_{\lambda=0} = \beta \left\langle \mathcal{H}_0 - \mathcal{H} \right\rangle^0$, where the superscript indicates expectation values with respect to $\mathcal{H}_0$. Setting $\lambda = 1$, we obtain

$$\ln Z \geq \ln Z(0) + \beta \left\langle \mathcal{H}_0 \right\rangle^0 - \beta \left\langle \mathcal{H} \right\rangle^0. \tag{V.73}$$

Eq.(V.73), known as the *Gibbs inequality*, is the basis for most variational estimates. Typically, the 'simpler' Hamiltonian $\mathcal{H}_0$ (and hence the right hand side of eq.(V.73)) includes several parameters $\{n_\alpha\}$. The best estimate for $\ln Z$ is obtained by finding the maximum of the right hand side with respect to these parameters. It can now be checked that the approximate evaluation of the grand partition function $\mathcal{Q}$ in the preceding section is equivalent to a variational treatment with $\mathcal{H}_0$ corresponding to a gas of hard-core particles of density n, for which (after replacing the sum by its dominant term)

$$\ln \mathcal{Q}_0 = \beta\mu N + \ln Z = V\left[n\left(1+\beta\mu-\ln(\lambda^3)\right) + n\ln\left(n^{-1}-\frac{\Omega}{2}\right)\right]. \tag{V.74}$$

The difference $\mathcal{H}-\mathcal{H}_0$ contains the attractive portion of the two body interactions. In the regions of phase space not excluded by the hard core interactions the gas in $\mathcal{H}_0$ is described by a uniform density n. Hence

$$\beta\left\langle \mathcal{H}_0-\mathcal{H}\right\rangle^0 = \beta V\frac{n^2}{2}u, \tag{V.75}$$

and

$$\beta P = \frac{\ln\mathcal{Q}}{V} \geq \left[n\left(1+\beta\mu-\ln(\lambda^3)\right) + n\ln\left(n^{-1}-\frac{\Omega}{2}\right)\right] + \frac{1}{2}\beta u n^2, \tag{V.76}$$

which is the same as eq.(V.66). The density n is now a parameter on the right hand side of eq.(V.76). Obtaining the best variational estimate by maximizing with respect to n is then equivalent to eq.(V.65).

V.G Corresponding States

We now have a good perturbative understanding of the behavior of a dilute interacting gas at high temperatures. At lower temperatures, attractive interactions lead to condensation into the liquid state. The qualitative behavior of the phase diagram is the same for most simple gases. There is a line of transitions in the coordinates (P,T) (corresponding to the coexistence of liquid and gas in the (V,T) plane) that terminates at a so called *critical point*. It is thus possible to transform a liquid to a gas without encountering any singularities. Since the ideal gas law is universal, i.e. independent of material, we may hope that there is also a generalized universal equation of state (presumably more complicated) that describes interacting gases, including liquid/gas condensation phenomena. This hope motivated the search for a law of *corresponding states*, obtained by appropriate

rescalings of state functions. The most natural choice of scales for pressure, volume, and temperature are those of the critical point, (P_c, V_c, T_c).

The van der Waals equation is an example of a generalized equation of state. Its critical point is found by setting $\partial P/\partial V|_T$ and $\partial^2 P/\partial V^2\big|_T$ to zero. The former is the limit of the flat coexistence portion of liquid/gas isotherms; the latter follows from the stability requirement $\kappa_T > 0$ (see the discussion after eq.(I.72)). The coordinates of the critical point are thus obtained from solving the following coupled equations,

$$\begin{cases} P = \dfrac{k_B T}{v-b} - \dfrac{a}{v^2} \\ \left.\dfrac{\partial P}{\partial v}\right|_T = -\dfrac{k_B T}{(v-b)^2} + \dfrac{2a}{v^3} = 0 \\ \left.\dfrac{\partial^2 P}{\partial v^2}\right|_T = \dfrac{2k_B T}{(v-b)^3} - \dfrac{6a}{v^4} = 0 \end{cases} , \tag{V.77}$$

where $v = V/N$ is the volume per particle. The solution to these equations is

$$\begin{cases} P_c = \dfrac{a}{27b^2} \\ v_c = 3b \\ k_B T_c = \dfrac{8a}{27b} \end{cases} . \tag{V.78}$$

Naturally, the critical point depends on the microscopic Hamiltonian (e.g. on the 2-body interaction) via the parameters a and b. However, we can scale out such dependencies by measuring P, T, and v in units of P_c, T_c and v_c. Setting $P_r = P/P_c$, $v_r = v/v_c$, and $T_r = T/T_c$, a reduced version of the van der Waals equation is obtained as

$$P_r = \frac{8}{3}\,\frac{T_r}{v_r - 1/3} - \frac{3}{v_r^2} \quad . \tag{V.79}$$

We have thus constructed a *universal* (material independent) equation of state. Since the original van der Waals equation depends only on *two* two parameters, eqs.(V.78) predict a universal dimensionless ratio,

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} = 0.375. \tag{V.80}$$

Experimentally, this ratio is found to be in the range of 0.28 to 0.33. The van der Waals equation is thus not a good candidate for the putative universal equation of state.

We can attempt to construct a generalized equation *empirically* by using *three* independent critical coordinates, and finding $P_r \equiv p_r(v_r, T_r)$ from the collapse of experimental data. Such an approach has some limited success in describing similar gases, e.g. the sequence of noble gases Ne, Xe, Kr, etc. However, different types of gases (e.g. diatomic, ionic, etc.) show rather different behaviors. This is not particularly surprising given the differences in the underlying Hamiltonians. We know rigorously from the virial expansion that perturbative treatment of the interacting gas does depend on the details of the microscopic potential. Thus the hope of finding a universal equation of state for all liquids and gases has no theoretical or experimental justification; each case has to be studied separately starting from its microscopic Hamiltonian. It is thus quite surprising that the collapse of experimental data does in fact work very well in the vicinity of the critical point, as described in the next section.

V.H Critical Point Behavior

To account for the universal behavior of gases close to their critical point, let us examine the isotherms in the vicinity of (P_c, v_c, T_c). For $T \geq T_c$, a Taylor expansion of $P(T, v)$ in the vicinity of v_c, for any T gives,

$$P(T,v) = P(T,v_c) + \left.\frac{\partial P}{\partial v}\right|_T (v-v_c) + \frac{1}{2}\left.\frac{\partial^2 P}{\partial v^2}\right|_T (v-v_c)^2 + \frac{1}{6}\left.\frac{\partial^3 P}{\partial v^3}\right|_T (v-v_c)^3 + \cdots . \quad \text{(V.81)}$$

Since $\partial P/\partial v|_T$ and $\partial^2 P/\partial v^2\big|_T$ are both zero at T_c, the expansion of the derivatives around the critical point gives

$$\begin{aligned}
P(T,v_c) &= P_c + \alpha(T-T_c) + \mathcal{O}\left[(T-T)^2\right] \\
\left.\frac{\partial P}{\partial v}\right|_{T,v_c} &= -a(T-T_c) + \mathcal{O}\left[(T-T_c)^2\right], \\
\left.\frac{\partial^2 P}{\partial v^2}\right|_{T,v_c} &= b(T-T_c) + \mathcal{O}\left[(T-T)^2\right], \\
\left.\frac{\partial^3 P}{\partial v^3}\right|_{T_c,v_c} &= -c + \mathcal{O}\left[(T-T_c)\right],
\end{aligned} \quad \text{(V.82)}$$

where a, b, and c are material dependent constants. The stability condition, $\delta P \delta v \leq 0$, requires $a > 0$ (for $T > T_c$) and $c > 0$ (for $T = T_c$), but provides no information on the sign of b. If an analytical expansion is possible, the isotherms of any gas in the vicinity of its critical point must have the general form,

$$P(T,v) = P_c + \alpha(T-T_c) - a(T-T_c)(v-v_C) + \frac{b}{2}(T-T_c)(v-v_c)^2 - \frac{c}{6}(v-v_c)^3 + \cdots . \quad \text{(V.83)}$$

Note that the third and fifth terms are of comparable magnitude for $(T - T_c) \sim (v - v_c)^2$. The fourth (and higher order terms) can then be neglected when this condition is satisfied.

• The analytic expansion of eq.(V.83) results in the following predictions for behavior close to the critical point:

(a) The gas compressibility diverges on approaching the critical point from the high temperature side, along the critical isochore ($v = v_c$) as,

$$\lim_{T \to T_c^+} \kappa(T, v_c) = -\frac{1}{v_c} \left. \frac{\partial P}{\partial v} \right|_T^{-1} = \frac{1}{v_c a (T - T_c)}. \tag{V.84}$$

(b) The critical isotherm ($T = T_c$) behaves as

$$P = P_c - \frac{c}{6}(v - v_c)^3 + \cdots. \tag{V.85}$$

(c) Eq.(V.83) is manifestly inapplicable to $T < T_c$. However, we can try to extract information for the low temperature side by applying the Maxwell construction to the unstable isotherms. Actually, dimensional considerations are sufficient to show that on approaching T_c from the low temperature side, the specific volumes of the coexisting liquid and gas phases approach each other as

$$\lim_{T \to T_c^-} (v_{\rm gas} - v_{\rm liquid}) \propto (T_c - T)^{1/2}. \tag{V.86}$$

The liquid–gas transition for $T < T_c$ is accompanied by a discontinuity in density, and the release of latent heat L. This kind of transition is usually referred to as *first order* or discontinuous. The difference between the two phases disappears as the line of first order transitions terminates at the critical point. The singular behavior at this point is attributed to a *second order* or continuous transition. Eq.(V.83) follows from no more than the constraints of mechanical stability, and the assumption of analytical isotherms. Although there are some unknown coefficients, eqs.(V.85)–(V.86) predict universal forms for the singularities close to the critical point and can be compared to experimental data. The experimental results do indeed confirm the general expectations of singular behavior, and there is universality in the results for different gases which can be summarized as

(a) The compressibility diverges on approaching the critical point as

$$\lim_{T \to T_c^+} \kappa(T, v_c) \propto (T - T_c)^{-\gamma}, \quad \text{with} \quad \gamma \approx 1.3 \quad . \tag{V.87}$$

(b) The critical isotherm behaves as

$$(P - P_c) \propto (v - v_c)^{\delta}, \quad \text{with} \quad \delta \approx 5.0 \quad . \tag{V.88}$$

(c) The difference between liquid and gas densities vanishes close to the critical point as

$$\lim_{T \to T_c^-} (\rho_{\text{liquid}} - \rho_{\text{gas}}) \propto \lim_{T \to T_c^-} (v_{\text{gas}} - v_{\text{liquid}}) \propto (T_c - T)^{\beta}, \quad \text{with} \quad \beta \approx 0.3 \quad . \tag{V.89}$$

These results clearly indicate that the assumption of analyticity of the isotherms, leading to eq.(V.83), is not correct. The exponents δ, γ, and β appearing in eqs.(V.88)–(V.89) are known as *critical indices*. Understanding the origin, universality, and numerical values of these exponents is the a fascinating subject explored in the modern theory of critical phenomena.

V.E Mean Field Theory of Condensation

In principle, all properties of the interacting system, including phase separation, are contained within the thermodynamic potentials that can be obtained by evaluating $Z(T,N)$ or $\mathcal{Q}(T,\mu)$. Phase transitions, however, are characterized by discontinuities in various state functions and must correspond to the appearance of singularities in the partition functions. At first glance, it is somewhat surprising that any singular behavior should emerge from computing such well behaved integrals (for short-ranged interactions) as

$$Z(T,N,V) = \int \frac{\prod_{i=1}^{N} d^3\vec{p}_i d^3\vec{q}_i}{N! h^{3N}} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta \sum_{i<j} \mathcal{V}(\vec{q}_i - \vec{q}_j) \right]. \tag{V.57}$$

Instead of evaluating the integrals perturbatively, we shall now set up a reasonable approximation scheme. The contributions of the hard core and attractive portions of the potential are again treated separately, and the partition function approximated by

$$Z(T,N,V) \approx \frac{1}{N!} \frac{1}{\lambda^{3N}} \underbrace{V\big(V-\Omega\big)\cdots\big(V-(N-1)\Omega\big)}_{\text{Excluded volume effects}} \exp(-\beta \bar{U}). \tag{V.58}$$

Here $\bar{U}$ represents an average attraction energy, obtained by assuming a *uniform density* $n = N/V$, as

$$\begin{aligned}\bar{U} =& \frac{1}{2}\sum_{i,j}\mathcal{V}_{\rm attr.}(\vec{q}_i - \vec{q}_j) = \frac{1}{2}\int d^3\vec{r}_1 d^3\vec{r}_2 n(\vec{r}_1) n(\vec{r}_2)\mathcal{V}_{\rm attr.}(\vec{r}_1 - \vec{r}_2) \\ \approx& \frac{n^2}{2} V \int d^3\vec{r}\,\mathcal{V}_{\rm attr.}(\vec{r}) \equiv -\frac{N^2}{2V}\,u.\end{aligned} \tag{V.59}$$

The parameter u describes the net effect of the attractive interactions. Substituting into eq.(V.58) leads to the following approximation for the partition function

$$Z(T,N,V) \approx \frac{(V - N\Omega/2)^N}{N!\lambda^{3N}} \exp\left[\frac{\beta u N^2}{2V}\right]. \tag{V.60}$$

From the resulting free energy,

$$F = -k_B T \ln Z = -N k_B T \ln(V - N\Omega/2) + N k_B T \ln(N/e) + 3N k_B T \ln\lambda - \frac{uN^2}{2V}, \tag{V.61}$$

we obtain the expression for the pressure in the canonical ensemble as

$$P_{\rm can} = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{N k_B T}{V - N\Omega/2} - \frac{uN^2}{2V^2}. \tag{V.62}$$

Remarkably, the uniform density approximation reproduces the van der Waals equation of state. However, the self-consistency of this approximation can now be checked. As long as κ_T is positive, eq.(V.54) implies that the variance of density vanishes for large volumes as $\langle n^2 \rangle_c = k_B T n^2 \kappa_T / V$. But κ_T diverges at T_c, and at lower temperatures its negativity implies an instability towards density fluctuations as discussed in the previous section. When condensation occurs, there is phase separation into high (liquid) and low (gas) density states, and the uniform density assumption becomes manifestly incorrect. This difficulty is circumvented in the *grand canonical ensemble*. Once the chemical potential is fixed, the number of particles (and hence density) in this ensemble is automatically adjusted to that of the appropriate phase.

As the assumption of a uniform density is correct for both the liquid and gas phases, we can use the approximations of eqs.(V.59) and (V.60) to estimate the grand partition function

$$\mathcal{Q}(T,\mu,V) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,N,V) \approx \sum_{N=0}^{\infty} \exp\left[N\ln\left(\frac{V}{N} - \frac{\Omega}{2}\right) + \frac{\beta u N^2}{2V} + \Delta N\right], \tag{V.63}$$

V.G Corresponding States

We now have a good perturbative understanding of the behavior of a dilute interacting gas at high temperatures. At lower temperatures, attractive interactions lead to condensation into the liquid state. The qualitative behavior of the phase diagram is the same for most simple gases. There is a line of transitions in the coordinates (P, T) (corresponding to the coexistence of liquid and gas in the (V, T) plane) that terminates at a so called *critical point*. It is thus possible to transform a liquid to a gas without encountering any singularities. Since the ideal gas law is universal, i.e. independent of material, we may hope that there is also a generalized universal equation of state (presumably more complicated) that describes interacting gases, including liquid/gas condensation phenomena. This hope motivated the search for a law of *corresponding states*, obtained by appropriate rescalings of state functions. The most natural choice of scales for pressure, volume, and temperature are those of the critical point, (P_c, V_c, T_c).

The van der Waals equation is an example of a generalized equation of state. Its critical point is found by setting $\partial P/\partial V|_T$ and $\partial^2 P/\partial V^2\big|_T$ to zero. The former is the limit of the flat coexistence portion of liquid/gas isotherms; the latter follows from the stability requirement $\kappa_T > 0$ (see the discussion after eq.(I.72)). The coordinates of the critical point are thus obtained from solving the following coupled equations,

$$\begin{cases} P = \dfrac{k_B T}{v-b} - \dfrac{a}{v^2} \\ \left.\dfrac{\partial P}{\partial v}\right|_T = -\dfrac{k_B T}{(v-b)^2} + \dfrac{2a}{v^3} = 0 \\ \left.\dfrac{\partial^2 P}{\partial v^2}\right|_T = \dfrac{2k_B T}{(v-b)^3} - \dfrac{6a}{v^4} = 0 \end{cases} , \tag{V.77}$$

where $v = V/N$ is the volume per particle. The solution to these equations is

$$\begin{cases} P_c = \dfrac{a}{27b^2} \\ v_c = 3b \\ k_B T_c = \dfrac{8a}{27b} \end{cases} . \tag{V.78}$$

Naturally, the critical point depends on the microscopic Hamiltonian (e.g. on the 2-body interaction) via the parameters a and b. However, we can scale out such dependencies by measuring P, T, and v in units of P_c, T_c and v_c. Setting $P_r = P/P_c$, $v_r = v/v_c$, and $T_r = T/T_c$, a reduced version of the van der Waals equation is obtained as

$$P_r = \frac{8}{3}\,\frac{T_r}{v_r - 1/3} - \frac{3}{v_r^2} \quad . \tag{V.79}$$

We have thus constructed a *universal* (material independent) equation of state. Since the original van der Waals equation depends only on *two* two parameters, eqs.(V.78) predict a universal dimensionless ratio,

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} = 0.375. \tag{V.80}$$

Experimentally, this ratio is found to be in the range of 0.28 to 0.33. The van der Waals equation is thus not a good candidate for the putative universal equation of state.

We can attempt to construct a generalized equation *empirically* by using *three* inde pendent critical coordinates, and finding $P_r \equiv p_r(v_r, T_r)$ from the collapse of experimental data. Such an approach has some limited success in describing similar gases, e.g. the sequence of noble gases Ne, Xe, Kr, etc. However, different types of gases (e.g. diatomic, ionic, etc.) show rather different behaviors. This is not particularly surprising given the differences in the underlying Hamiltonians. We know rigorously from the virial expansion that perturbative treatment of the interacting gas does depend on the details of the mi croscopic potential. Thus the hope of finding a universal equation of state for all liquids and gases has no theoretical or experimental justification; each case has to be studied separately starting from its microscopic Hamiltonian. It is thus quite surprising that the collapse of experimental data does in fact work very well in the vicinity of the critical point, as described in the next section.

V.H Critical Point Behavior

To account for the universal behavior of gases close to their critical point, let us examine the isotherms in the vicinity of (P_c, v_c, T_c). For $T \geq T_c$, a Taylor expansion of $P(T, v)$ in the vicinity of v_c, for any T gives,

$$P(T,v) = P(T,v_c) + \left.\frac{\partial P}{\partial v}\right|_T (v-v_c) + \frac{1}{2}\left.\frac{\partial^2 P}{\partial v^2}\right|_T (v-v_c)^2 + \frac{1}{6}\left.\frac{\partial^3 P}{\partial v^3}\right|_T (v-v_c)^3 + \cdots. \quad \text{(V.81)}$$

Since $\partial P/\partial v|_T$ and $\partial^2 P/\partial v^2\big|_T$ are both zero at T_c, the expansion of the derivatives around the critical point gives

$$\begin{aligned}
P(T,v_c) &= P_c + \alpha(T-T_c) + \mathcal{O}\left[(T-T)^2\right] \\
\left.\frac{\partial P}{\partial v}\right|_{T,v_c} &= -a(T-T_c) + \mathcal{O}\left[(T-T_c)^2\right], \\
\left.\frac{\partial^2 P}{\partial v^2}\right|_{T,v_c} &= b(T-T_c) + \mathcal{O}\left[(T-T)^2\right], \\
\left.\frac{\partial^3 P}{\partial v^3}\right|_{T_c,v_c} &= -c + \mathcal{O}\left[(T-T_c)\right],
\end{aligned} \quad \text{(V.82)}$$

where a, b, and c are material dependent constants. The stability condition, $\delta P \delta v \leq 0$, requires $a > 0$ (for $T > T_c$) and $c > 0$ (for $T = T_c$), but provides no information on the sign of b. If an analytical expansion is possible, the isotherms of any gas in the vicinity of its critical point must have the general form,

$$P(T,v) = P_c + \alpha(T-T_c) - a(T-T_c)(v-v_C) + \frac{b}{2}(T-T_c)(v-v_c)^2 - \frac{c}{6}(v-v_c)^3 + \cdots. \quad \text{(V.83)}$$

Note that the third and fifth terms are of comparable magnitude for $(T - T_c) \sim (v - v_c)^2$. The fourth (and higher order terms) can then be neglected when this condition is satisfied.

• The analytic expansion of eq.(V.83) results in the following predictions for behavior close to the critical point:

(a) The gas compressibility diverges on approaching the critical point from the high temperature side, along the critical isochore ($v = v_c$) as,

$$\lim_{T \to T_c^+} \kappa(T, v_c) = -\frac{1}{v_c} \left. \frac{\partial P}{\partial v} \right|_T^{-1} = \frac{1}{v_c a (T - T_c)}. \tag{V.84}$$

(b) The critical isotherm ($T = T_c$) behaves as

$$P = P_c - \frac{c}{6}(v - v_c)^3 + \cdots. \tag{V.85}$$

(c) Eq.(V.83) is manifestly inapplicable to $T < T_c$. However, we can try to extract information for the low temperature side by applying the Maxwell construction to the unstable isotherms. Actually, dimensional considerations are sufficient to show that on approaching T_c from the low temperature side, the specific volumes of the coexisting liquid and gas phases approach each other as

$$\lim_{T \to T_c^-} (v_{\rm gas} - v_{\rm liquid}) \propto (T_c - T)^{1/2}. \tag{V.86}$$

The liquid–gas transition for $T < T_c$ is accompanied by a discontinuity in density, and the release of latent heat L. This kind of transition is usually referred to as *first order* or discontinuous. The difference between the two phases disappears as the line of first order transitions terminates at the critical point. The singular behavior at this point is attributed to a *second order* or continuous transition. Eq.(V.83) follows from no more than the constraints of mechanical stability, and the assumption of analytical isotherms. Although there are some unknown coefficients, eqs.(V.85)–(V.86) predict universal forms for the singularities close to the critical point and can be compared to experimental data. The experimental results do indeed confirm the general expectations of singular behavior, and there is universality in the results for different gases which can be summarized as

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(b) The critical isotherm behaves as

$$(P - P_c) \propto (v - v_c)^{\delta}, \quad \text{with} \quad \delta \approx 5.0 \quad . \tag{V.88}$$

(c) The difference between liquid and gas densities vanishes close to the critical point as

$$\lim_{T \to T_c^-} (\rho_{\text{liquid}} - \rho_{\text{gas}}) \propto \lim_{T \to T_c^-} (v_{\text{gas}} - v_{\text{liquid}}) \propto (T_c - T)^{\beta}, \quad \text{with} \quad \beta \approx 0.3 \quad . \tag{V.89}$$

These results clearly indicate that the assumption of analyticity of the isotherms, leading to eq.(V.83), is not correct. The exponents δ, γ, and β appearing in eqs.(V.88)–(V.89) are known as *critical indices*. Understanding the origin, universality, and numerical values of these exponents is the a fascinating subject explored in the modern theory of critical phenomena.

VI. Quantum Statistical Mechanics

There are limitations to the applicability of classical statistical mechanics. The need to include quantum mechanical effects becomes specially apparent at low temperatures. In this section we shall first demonstrate the failure of the classical results in the contexts of heat capacities of molecular gases and solids, and the ultra-violet catastrophe in black body radiation. We shall then reformulate statistical mechanics using quantum concepts.

VI.A Dilute Polyatomic Gases

Consider a dilute gas of polyatomic molecules. The Hamiltonian for *each* molecule of n atoms is

$$\mathcal{H}_1 = \sum_{i=1}^{n} \frac{\vec{p}_i^{\,2}}{2m} + \mathcal{V}(\vec{q}_1, \ldots, \vec{q}_n), \tag{VI.1}$$

where the potential energy $\mathcal{V}$, contains all the information on molecular bonds. For simplicity, we have assumed that all atoms in the molecule have the same mass. If the masses are different, the Hamiltonian can be brought into the above form by rescaling the coordinates $\vec{q}_i$ by $\sqrt{m_i/m}$ (and the momenta by $\sqrt{m/m_i}$), where m_i is the mass of the $i^{\rm th}$ atom. Ignoring the interactions *between* molecules, the partition function of a dilute gas is

$$Z(N) = \frac{Z_1^N}{N!} = \frac{1}{N!}\left\{ \int \prod_{i=1}^{n} \frac{d^3\vec{p}_i d^3\vec{q}_i}{h^3} \ \exp\left[-\beta \sum_{i=1}^{n} \frac{\vec{p}_i^{\,2}}{2m} - \beta \mathcal{V}(\vec{q}_1, \ldots, \vec{q}_n) \right] \right\}^N . \tag{VI.2}$$

The chemical bonds that keep the molecule together are usually quite strong (energies of the order of electron volts). At typical accessible temperatures, which are much smaller than the corresponding dissociation temperatures ($\approx 10^4\,^\circ K$), the molecule has a well defined shape and only undergoes small deformations. The contribution of these deformations to the one particle partition function Z_1, can be computed as follows:

(a) The first step is to find the equilibrium positions, $(\vec{q}_1^{\,*}, \ldots, \vec{q}_n^{\,*})$, by minimizing the potential $\mathcal{V}$.

(b) The energy cost of small deformations about equilibrium is then obtained by setting $\vec{q}_i = \vec{q}_i^{\,*} + \vec{u}_i$, and making an expansion in powers of $\vec{u}$,

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2} \sum_{i,j=1}^{n} \sum_{\alpha,\beta=1}^{3} \frac{\partial^2 \mathcal{V}}{\partial q_{i,\alpha} \partial q_{j,\beta}} \ u_{i,\alpha} u_{j,\beta} + \mathcal{O}(u^3). \tag{VI.3}$$

(Here $i, j = 1, \cdots, n$, identify the atoms, and $\alpha, \beta = 1, 2, 3$ label a particular component.) Since the expansion is around a stable equilibrium configuration, the first derivatives are absent in eq.(VI.3), and the matrix of second derivatives is *positive definite*, i.e. it has only non-negative eigenvalues.

(c) The *normal modes* of the molecule are obtained by diagonalizing the $3n \times 3n$ matrix $\partial^2 \mathcal{V}/\partial q_{i,\alpha} \partial q_{j,\beta}$. The resulting $3n$ eigenvalues K_s, indicate the *stiffness* of each mode. We can change variables from the original deformations $\{\vec{u}_i\}$, to the amplitudes $\{\tilde{u}_s\}$, of the eigenmodes. The corresponding conjugate momenta are $\tilde{p}_s = m\dot{\tilde{u}}_s$. Since the transformation from $\{\vec{u}_i\}$ to $\{\tilde{u}_s\}$ is *unitary* (preserving the length of a vector), $\sum_i \vec{p}_i{}^2 = \sum_s \tilde{p}_s^2$, and the quadratic part of the resulting deformation Hamiltonian is

$$\mathcal{H}_1 = \mathcal{V}^* + \sum_{s=1}^{3n} \left[\frac{1}{2m} \tilde{p}_s^2 + \frac{K_s}{2} \tilde{u}_s^2 \right]. \tag{VI.4}$$

(Such transformations are also *canonical*, preserving the measure of integration in phase space, $\prod_{i,\alpha} du_{i,\alpha} dp_{i,\alpha} = \prod_s d\tilde{u}_s d\tilde{p}_s$.)

The average energy of each molecule is the expectation value of the above Hamiltonian. Since each quadratic degree of freedom classically contributes a factor of $k_B T/2$ to the energy,

$$\langle \mathcal{H}_1 \rangle = \mathcal{V}^* + \frac{3n+m}{2} k_B T. \tag{VI.5}$$

Only modes with a finite stiffness can store potential energy, and m is defined as the number such modes with non-zero K_s. The following symmetries of the potential force some eigenvalues to zero:

(a) *Translation symmetry:* Since $\mathcal{V}(\vec{q}_1 + \vec{c}, \cdots, \vec{q}_n + \vec{c}) = \mathcal{V}(\vec{q}_1, \cdots, \vec{q}_n)$, no energy is stored the center of mass coordinate $\vec{Q} = \sum_\alpha \vec{q}_\alpha/n$, i.e. $\mathcal{V}(\vec{Q}) = \mathcal{V}(\vec{Q} + \vec{c})$, and the corresponding three values of $K_{\rm trans}$ are zero.

(b) *Rotation symmetry:* There is also no potential energy associated with rotations of the molecule, and $K_{\rm rot} = 0$ for the corresponding stiffnesses. The number of rotational modes, $0 \leq r \leq 3$, depends on the shape of the molecule; for example, a rod shaped molecule has $r = 2$, as a rotation parallel to its axis does not result in a new configuration.

The remaining $m = 3n - 3 - r$ eigenvectors of the matrix have non-zero stiffness, and correspond to the *vibrational* normal modes. The energy per molecule, from eq.(VI.5), is thus

$$\langle \mathcal{H}_1 \rangle = \frac{6n - 3 - r}{2} k_B T. \tag{VI.6}$$

The corresponding heat capacities,

$$C_V = \frac{(6n-3-r)}{2}k_B, \quad \text{and} \quad C_P = C_V + k_B = \frac{(6n-1-r)}{2}k_B, \tag{VI.7}$$

are temperature independent. The ratio $\gamma = C_P/C_V$ is easily measured in adiabatic processes. Values of γ, expected on the basis of the above argument, are listed below for a number of different molecules.

Monatomic	He	$n=1$	$r=0$	$\gamma = 5/3$
Diatomic	O_2 or CO	$n=2$	$r=2$	$\gamma = 9/7$
Linear triatomic	O–C–O	$n=3$	$r=2$	$\gamma = 15/13$
Planar triatomic	$\mathrm{H}/^{\mathrm{O}}\backslash\mathrm{H}$	$n=3$	$r=3$	$\gamma = 14/12 = 7/6$
Tetra-atomic	NH_3	$n=4$	$r=3$	$\gamma = 20/18 = 10/9$

Measurements of the heat capacity of dilute gases do not agree with the above predictions. For example, the value $C_V/k_B = 7/2$, for a diatomic gas such as oxygen, is only observed at temperatures higher than a few thousand degrees Kelvin. At room temperatures, a lower value of $5/2$ is observed, while at even lower temperatures of around $10^0 K$, it is further reduced to $3/2$. The low temperature value is similar to that of a monatomic gas, and suggests that no energy is stored in the rotational and vibrational degrees of freedom. These observations can be explained if the allowed energy levels are *quantized*.

• **Vibrational modes:** A diatomic molecule has one vibrational mode with stiffness $K \equiv m\omega^2$, where ω is the frequency of oscillations. The classical partition function for this mode is

$$\begin{aligned} Z^c_{\rm vib} &= \int \frac{dp\,dq}{h}\ \exp\left[-\beta\left(\frac{p^2}{2m}+\frac{m\omega^2 q^2}{2}\right)\right] \\ &= \frac{1}{h}\sqrt{\left(\frac{2\pi m}{\beta}\right)\left(\frac{2\pi}{\beta m\omega^2}\right)} = \frac{2\pi}{h\beta\omega} = \frac{k_B T}{\hbar\omega}, \end{aligned} \tag{VI.8}$$

where $\hbar = h/2\pi$. The corresponding energy stored in this mode,

$$\langle \mathcal{H}_{\rm vib}\rangle^c = -\frac{\partial \ln Z}{\partial\beta} = \frac{\partial \ln(\beta\hbar\omega)}{\partial\beta} = \frac{1}{\beta} = k_B T, \tag{VI.9}$$

comes from $k_B T/2$ per kinetic and potential degrees of freedom. In quantum mechanics, the allowed values of energy are quantized such that

$$\mathcal{H}^q_{\rm vib} = \hbar\omega\left(n+\frac{1}{2}\right), \tag{VI.10}$$

with $n = 0, 1, 2, \cdots$. Assuming that the probability of each discrete level is proportional to its Boltzmann weight (as will be justified later on), there is a normalization factor

$$Z^q_{\rm vib} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}. \tag{VI.11}$$

The high temperature limit,

$$\lim_{\beta\to 0} Z^q_{\rm vib} = \frac{1}{\beta\hbar\omega} = \frac{k_B T}{\hbar\omega},$$

coincides with eq.(VI.8)(due in part to the choice of h as the measure of classical phase space).

The expectation value of vibrational energy is

$$E^q_{\rm vib} = -\frac{\partial \ln Z}{\partial\beta} = \frac{\hbar\omega}{2} + \frac{\partial}{\partial\beta}\ln(1-e^{-\beta\hbar\omega}) = \frac{\hbar\omega}{2} + \hbar\omega\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}. \tag{VI.12}$$

The first term is the energy cost of *quantum fluctuations* that are present even in the zero temperature ground state. The second term describes the additional energy due to *thermal fluctuations*. The resulting heat capacity,

$$C^q_{\rm vib} = \frac{dE^q_{\rm vib}}{dT} = k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}, \tag{VI.13}$$

achieves the classical value of k_B only at temperatures $T \gg \theta_{\rm vib}$, where $\theta_{\rm vib} = \hbar\omega/k_B$ is a characteristic temperature associated with the quanta of vibrational energy. For $T \ll \theta_{\rm vib}$, $C^q_{\rm vib}$ goes to zero as $\exp(-\theta_{\rm vib}/T)$. Typical values of $\theta_{\rm vib}$ are in the range of 10^3 to 10^4 degrees Kelvin, explaining why the classical value of heat capacity is observed only at higher temperatures.

• **Rotational modes:** To account for the low temperature anomaly in the heat capacity of diatomic molecules, we have to study the quantization of the rotational degrees of freedom. Classically, the orientation of a diatomic molecule is specified by two angles θ and ϕ, and its Lagrangian (equal to the kinetic energy) is

$$\mathcal{L} = \frac{I}{2}\left(\dot\theta^2 + \sin^2\theta\ \dot\phi^2\right), \tag{VI.14}$$

where I is the moment of inertia. In terms of the conjugate momenta,

$$p_\theta = \frac{\partial\mathcal{L}}{d\dot\theta} = I\dot\theta\ , \quad p_\phi = \frac{\partial\mathcal{L}}{d\dot\phi} = I\sin^2\theta\ \dot\phi, \tag{VI.15}$$

the Hamiltonian for rotations is

$$\mathcal{H}_{\rm rot} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) \equiv \frac{\vec{L}^2}{2I}, \tag{VI.16}$$

where $\vec{L}$ is the angular momentum. From the classical partition function,

$$\begin{aligned} Z^c_{\rm rot} &= \frac{1}{h^2}\int_0^\pi d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dp_\theta dp_\phi \exp\left[-\frac{\beta}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)\right] \\ &= \left(\frac{2\pi I}{\beta}\right)\left(\frac{4\pi}{h^2}\right) = \frac{2Ik_BT}{\hbar^2}, \end{aligned} \tag{VI.17}$$

the stored energy is

$$\langle E_{\rm rot}\rangle^c = -\frac{\partial \ln Z}{\partial\beta} = \frac{\partial}{\partial\beta}\ln\left(\frac{\beta\hbar^2}{2I}\right) = k_BT, \tag{VI.18}$$

as expected for two degrees of freedom. In quantum mechanics, the allowed values of angular momentum are quantized to $\vec{L}^2 = \hbar^2\ell(\ell+1)$ with $\ell = 0, 1, 2, \cdots$, and each state has a degeneracy of $2\ell+1$ (along a selected direction, $L_z = -\ell, \cdots, +\ell$). A partition function is now obtained for these levels as

$$Z^q_{\rm rot} = \sum_{\ell=0}^{\infty} \exp\left[-\frac{\beta\hbar^2\ell(\ell+1)}{2I}\right](2\ell+1) = \sum_{\ell=0}^{\infty}\exp\left[-\frac{\theta_{\rm rot}\ell(\ell+1)}{T}\right](2\ell+1), \tag{VI.19}$$

where $\theta_{\rm rot} = \hbar^2/(2Ik_B)$ is a characteristic temperature associated with quanta of rotational energy. While the sum can not be analytically evaluated in general, we can study its high and low temperature limits:

(a) For $T \gg \theta_{\rm rot}$, the terms in eq.(VI.19) vary slowly, and the sum can be replaced by the integral

$$\begin{aligned} \lim_{T\to\infty} Z^q_{\rm rot} &= \int_0^\infty dx(2x+1)\ \exp\left[-\frac{\theta_{\rm rot}\, x(x+1)}{T}\right] \\ &= \int_0^\infty dy\ e^{-\theta_{\rm rot}y/T} = \frac{T}{\theta_{\rm rot}} = Z^c_{\rm rot}, \end{aligned} \tag{VI.20}$$

i.e. the classical result of eq.(VI.17) is recovered.

(b) For $T \ll \theta_{\rm rot}$, the first few terms dominate the sum, and

$$\lim_{T\to\infty} Z^q_{\rm rot} = 1 + 3e^{-2\theta_{\rm rot}/T} + \mathcal{O}(e^{-6\theta_{\rm rot}/T}), \tag{VI.21}$$

leading to an energy

$$E^q_{\rm rot} = -\frac{\partial \ln Z}{\partial \beta} \approx -\frac{\partial}{\partial \beta} \ln \left[1 + 3e^{-2\theta_{\rm rot}/T}\right] \approx 6k_B\theta_{\rm rot} e^{-2\theta_{\rm rot}/T}. \tag{VI.22}$$

The resulting heat capacity vanishes at low temperatures as

$$C_{\rm rot} = \frac{dE^q_{\rm rot}}{dT} = 3k_B \left(\frac{2\theta_{\rm rot}}{T}\right)^2 e^{-2\theta_{\rm rot}/T} + \cdots. \tag{VI.23}$$

Typical values of $\theta_{\rm rot}$ are between 1 and 10 $^\circ K$, explaining the lower temperature shoulder in the heat capacity measurements. At very low temperatures, the only contributions come from the kinetic energy of the center of mass, and the molecule behaves as a monatomic particle. (The heat capacity vanishes at even lower temperatures due to quantum statistics, as will be discussed in the context of identical particles.)

VI.B Vibrations of a Solid

Attractive interactions between particles first lead to condensation from a gas to liquid at low temperatures, and finally cause freezing into a solid state at even lower temperatures. For the purpose of discussing its thermodynamics, the solid can be regarded as a very large molecule subject to a Hamiltonian similar to eq.(VI.1), with $n = N \gg 1$ atoms. We can then proceed with the steps outlined in the previous section.

(a) The classical ground state configuration of the solid is obtained by minimizing the potential $\mathcal{V}$. In almost all cases, the minimum energy corresponds to a periodic arrangement of atoms forming a *lattice*. In terms of the three *basis vectors*, $\hat{a}$, $\hat{b}$, and $\hat{c}$, the locations of atoms in a simple crystal are given by

$$\vec{q}^{\,*}(\ell, m, n) = \left[\ell\hat{a} + m\hat{b} + n\hat{c}\right] \equiv \vec{r}, \tag{VI.24}$$

where $\{\ell, m, n\}$ is a triplet of integers.

(b) At finite temperatures, the atoms may undergo small deformations

$$\vec{q}_{\vec{r}} = \vec{r} + \vec{u}(\vec{r}), \tag{VI.25}$$

with a cost in potential energy of

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2} \sum_{\substack{\vec{r},\vec{r}\,' \\ \alpha,\beta}} \frac{\partial^2 \mathcal{V}}{\partial q_{\vec{r},\alpha} \partial q_{\vec{r}\,',\beta}} u_\alpha(\vec{r})\; u_\beta(\vec{r}\,') + O(u^3). \tag{VI.26}$$

(c) Finding the normal modes of a crystal is considerably simplified by its *translational symmetry*. In particular, the matrix of second derivatives only depends on the *relative* separation of two points,

$$\frac{\partial^2 \mathcal{V}}{\partial q_{\vec{r},\alpha} \partial q_{\vec{r}\,',\beta}} = K_{\alpha\beta}(\vec{r} - \vec{r}\,'). \tag{VI.27}$$

It is always possible to take advantage of such a symmetry to at least partially diagonalize the matrix by using a *Fourier basis*,

$$u_\alpha(\vec{r}) = {\sum_{\vec{k}}}' \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{N}} \tilde{u}_\alpha(\vec{k}\,). \tag{VI.28}$$

The sum is restricted to *wavevectors* $\vec{k}$ inside a *Brillouin zone*. For example, in a cubic lattice of spacing a, each component of $\vec{k}$ is restricted to the interval $[-\pi/a, \pi/a]$. This is because wavevectors outside this interval carry no additional information as $(k_x + 2\pi m/a)(na) = k_x(na) + 2mn\pi$, and any phase that is a multiple of 2π does not effect the sum in eq.(VI.28). In terms of the Fourier modes, the potential energy of deformations is

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2N} \sum_{\substack{(\vec{r},\vec{r}\,'),(\vec{k},\vec{k}\,') \\ \alpha,\beta}} K_{\alpha\beta}(\vec{r} - \vec{r}\,') e^{i\vec{k}\cdot\vec{r}} \tilde{u}_\alpha(\vec{k}\,) e^{i\vec{k}\,'\cdot\vec{r}\,'} \tilde{u}_\beta(\vec{k}\,'). \tag{VI.29}$$

We can change variables to relative and center of mass coordinates,

$$\vec{\rho} = \vec{r} - \vec{r}\,', \quad \text{and} \quad \vec{R} = \frac{\vec{r} + \vec{r}\,'}{2},$$

by setting

$$\vec{r} = \vec{R} + \frac{\vec{\rho}}{2}, \quad \text{and} \quad \vec{r}\,' = \vec{R} - \frac{\vec{\rho}}{2}.$$

Eq.(VI.29) now simplifies to

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2N} \sum_{\substack{\vec{k},\vec{k}\,' \\ \alpha,\beta}} \left(\sum_{\vec{R}} e^{i(\vec{k}+\vec{k}\,')\cdot\vec{R}} \right) \left(\sum_{\vec{\rho}} K_{\alpha\beta}(\vec{\rho}) e^{i(\vec{k}-\vec{k}\,')\cdot\vec{\rho}/2} \tilde{u}_\alpha(\vec{k}\,) \tilde{u}_\beta(\vec{k}\,') \right). \tag{VI.30}$$

As the sum in the first brackets is $N\delta_{\vec{k}+\vec{k}',0}$,

$$\begin{aligned} \mathcal{V} &= \mathcal{V}^* + \frac{1}{2} \sum_{\vec{k},\alpha,\beta} \left[\sum_{\vec{\rho}} K_{\alpha\beta}(\vec{\rho}) e^{i\vec{k}\cdot\vec{\rho}} \right] \tilde{u}_\alpha(\vec{k}\,) \tilde{u}_\beta(-\vec{k}\,) \\ &= \mathcal{V}^* + \frac{1}{2} \sum_{\vec{k},\alpha,\beta} \tilde{K}_{\alpha\beta}(\vec{k}\,) \tilde{u}_\alpha(\vec{k}\,) \tilde{u}_\beta(\vec{k}\,)^*, \end{aligned} \tag{VI.31}$$

where $\tilde{K}_{\alpha\beta}(\vec{k}\,) = \sum_{\vec{\rho}} K_{\alpha\beta}(\vec{\rho}\,) \exp(i\vec{k}\cdot\vec{\rho}\,)$, and $\tilde{u}_\beta(\vec{k}\,)^* = \tilde{u}_\beta(-\vec{k}\,)$ is the complex conjugate of $\tilde{u}_\beta(\vec{k}\,)$.

The different Fourier modes are thus decoupled at the quadratic order, and the task of diagonalizing the $3N \times 3N$ matrix of second derivatives is reduced to diagonalizing the 3×3 matrix $\tilde{K}_{\alpha\beta}(\vec{k}\,)$ separately for each $\vec{k}$. The from of $\tilde{K}_{\alpha\beta}$ is further restricted by the point group symmetries of the crystal. The discussion of such constraints is beyond the intent of this section and for simplicity we shall assume that $\tilde{K}_{\alpha\beta}(\vec{k}\,) = \delta_{\alpha,\beta}\tilde{K}(\vec{k}\,)$, is already diagonal. (For an isotropic material, this implies a specific relation between bulk and shear moduli.)

The kinetic energy of deformations is

$$\sum_{i=1}^{N} \frac{m}{2}\dot{\vec{q}}_i^{\,2} = \sum_{\vec{k},\alpha} \frac{m}{2}\dot{\tilde{u}}_\alpha(\vec{k}\,)\dot{\tilde{u}}_\alpha(\vec{k}\,)^* = \sum_{\vec{k},\alpha} \frac{1}{2m}\tilde{p}_\alpha(\vec{k}\,)\tilde{p}_\alpha(\vec{k}\,)^*, \tag{VI.32}$$

where

$$\tilde{p}_\alpha(\vec{k}\,) = \frac{\partial \mathcal{L}}{\partial \dot{\tilde{u}}_\alpha(\vec{k}\,)} = m\dot{\tilde{u}}_\alpha(\vec{k}\,),$$

is the momentum conjugate to $\tilde{u}_\alpha(\vec{k}\,)$. The resulting deformation Hamiltonian,

$$\mathcal{H} = \mathcal{V}^* + \sum_{\vec{k},\alpha} \left[\frac{1}{2m} \left| \tilde{p}_\alpha\left(\vec{k}\,\right) \right|^2 + \frac{\tilde{K}(\vec{k}\,)}{2} \left| \tilde{u}_\alpha\left(\vec{k}\,\right) \right|^2 \right], \tag{VI.33}$$

describes $3N$ independent harmonic oscillators of frequencies $\omega_\alpha(\vec{k}\,) = \sqrt{\tilde{K}(\vec{k}\,)/m}$.

In a classical treatment, each harmonic oscillator of non-zero stiffness contributes $k_B T$ to the internal energy of the solid. At most, 6 of the $3N$ oscillators are expected to have zero stiffness (corresponding to uniform translations and rotations of the crystal). Thus, up to non-extensive corrections of order $1/N$, the classical internal energy associated with Hamiltonian (VI.33) is $3Nk_BT$, leading to a temperature independent heat capacity of $3k_B$ per atom. In fact, the measured heat capacity vanishes at low temperatures. We can again relate this observation to the quantization of the energy levels of each oscillator, as discussed in the previous section. Quantizing each harmonic mode separately, gives the allowed values of the Hamiltonian as

$$\mathcal{H}^q = \mathcal{V}^* + \sum_{\vec{k},\alpha} \hbar\omega_\alpha(\vec{k}\,) \left(n_{\vec{k},\alpha} + \frac{1}{2} \right), \tag{VI.34}$$

where the set of integers $\{n_{\vec{k},\alpha}\}$ describes the quantum micro-state of the oscillators. Since the oscillators are independent, their partition function,

$$Z^q = \sum_{\{n_{\vec{k},\alpha}\}} e^{-\beta \mathcal{H}^q} = e^{-\beta E_0} \prod_{\vec{k},\alpha} \sum_{n_{\vec{k},\alpha}} e^{-\beta \hbar \omega_\alpha(\vec{k}) n_{\vec{k},\alpha}} = e^{-\beta E_0} \prod_{\vec{k},\alpha} \left[\frac{1}{1 - e^{-\beta \hbar \omega_\alpha(\vec{k})}} \right], \quad \text{(VI.35)}$$

is the product of single oscillator partition functions such as eq.(VI.11). (E_0 includes the ground state energies of all oscillators in addition to $\mathcal{V}^*$.)

The internal energy is

$$E(T) = \langle \mathcal{H}^q \rangle = E_0 + \sum_{\vec{k},\alpha} \hbar \omega_\alpha(\vec{k}) \left\langle n_\alpha(\vec{k}) \right\rangle, \quad \text{(VI.36)}$$

where the average *occupation numbers* are given by

$$\begin{aligned} \left\langle n_\alpha(\vec{k}) \right\rangle &= \frac{\sum_{n=0}^{\infty} n e^{-\beta \hbar \omega_\alpha(\vec{k}) n}}{\sum_{n=0}^{\infty} e^{-\beta \hbar \omega_\alpha(\vec{k}) n}} = -\frac{\partial}{\partial(\beta \hbar \omega_\alpha(\vec{k}))} \ln \left(\frac{1}{1 - e^{-\beta \hbar \omega_\alpha(\vec{k})}} \right) \\ &= \frac{e^{-\beta \hbar \omega_\alpha(\vec{k})}}{1 - e^{-\beta \hbar \omega_\alpha(\vec{k})}} = \frac{1}{e^{\beta \hbar \omega_\alpha(\vec{k})} - 1}. \end{aligned} \quad \text{(VI.37)}$$

As a first attempt at including quantum mechanical effects, we may adopt the *Einstein model* in which all the oscillators are assumed to have the same frequency ω_E. This model corresponds to atoms that are pinned to their ideal location by springs of stiffness $\bar{K} = \partial^2 \mathcal{V}/\partial q^2 = m\omega_E^2$. The resulting internal energy,

$$E = E_0 + 3N \frac{\hbar \omega_E e^{-\beta \hbar \omega_E}}{1 - e^{-\beta \hbar \omega_E}}, \quad \text{(VI.38)}$$

and heat capacity,

$$C = \frac{dE}{dT} = 3Nk_B \left(\frac{T_E}{T} \right)^2 \frac{e^{-T_E/T}}{\left(1 - e^{-T_E/T}\right)^2}, \quad \text{(VI.39)}$$

is simply proportional to that of a single oscillator (eqs.(VI.12) and (VI.13)). In particular, there is an exponential decay of the heat capacity to zero with a characteristic temperature $T_E = \hbar \omega_E / k_B$. However, the experimentally measured heat capacity decays to zero much more slowly, as T^3.

The discrepancy is resolved through the *Debye model*, which emphasizes that at low temperatures the main contribution to heat capacity is from the oscillators of lowest frequency that are the most easily excited. The lowest energy modes in turn correspond to smallest wavevectors $k = |\vec{k}|$, or longest wavelengths $\lambda = 2\pi/k$. Indeed, the modes with

$\vec{k} = 0$ simply describe pure translations of the lattice and have zero stiffness. By continuity we expect, $\lim_{\vec{k}\to 0} \tilde{K}(\vec{k}\,) = 0$, and ignoring considerations of crystal symmetry, the expansion of $\tilde{K}(\vec{k}\,)$ at small wavevectors takes the form

$$\tilde{K}(\vec{k}\,) = Bk^2 + \mathcal{O}(k^4).$$

The odd terms are absent in the expansion, since $\tilde{K}(\vec{k}\,) = \tilde{K}(-\vec{k}\,)$ follows from $K(\vec{r}-\vec{r}\,') = K(\vec{r}\,' - \vec{r}\,)$ in real space. The corresponding frequencies at long wavelengths are

$$\omega(\vec{k}\,) = \sqrt{\frac{Bk^2}{m}} = vk, \tag{VI.40}$$

where $v = \sqrt{B/m}$ is the *speed of sound* in the crystal. (In a real material, $\tilde{K}_{\alpha\beta}$ is not proportional to $\delta_{\alpha\beta}$, and different *polarizations* of sound have different velocities.)

The quanta of vibrational modes are usually referred to as *phonons*. Using the *dispersion* relation in eq.(VI.40), the contribution of phonons to the internal energy is

$$\langle \mathcal{H}^q \rangle = E_0 + \sum_{\vec{k},\alpha} \frac{\hbar v k}{e^{\beta\hbar v k} - 1}. \tag{VI.41}$$

With *periodic boundary conditions* in a box of dimensions $L_x \times L_y \times L_z$, the allowed wavevectors are

$$\vec{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right), \tag{VI.42}$$

where n_x, n_y, and n_z are integers. In the large size limit, these modes are very densely packed, and the number of modes in a volume element $d^3\vec{k}$ is

$$d\mathcal{N} = \frac{dk_x}{2\pi/L_x}\,\frac{dk_y}{2\pi/L_y}\,\frac{dk_x}{2\pi/L_z} = \frac{V}{(2\pi)^3}\,d^3\vec{k} \equiv \rho d^3\vec{k}. \tag{VI.43}$$

Using the *phase space density* ρ, any sum over allowed wavevectors can be replaced by an integral as

$$\lim_{V\to\infty} \sum_{\vec{k}} f(\vec{k}\,) = \int d^3\vec{k}\,\rho f(\vec{k}\,). \tag{VI.44}$$

Hence, eq.(VI.41) can be re-written as

$$E = E_0 + 3V \int^{\text{B.Z.}} \frac{d^3\vec{k}}{(2\pi)^3}\,\frac{\hbar v k}{e^{\beta\hbar v k} - 1}, \tag{VI.45}$$

where the integral is performed over the volume of the Brillouin zone, and the factor of 3 comes from assuming the same sound velocity for the three polarizations.

Due to its dependence on the shape of the Brillouin zone, it is not possible to give a simple closed form expression for the energy in eq.(VI.45). However, we can examine its high and low temperature limits. The characteristic temperature separating the two limits,

$$T_D = \frac{\hbar v k_{\max}}{k_B} \approx \frac{\hbar v}{k_B} \cdot \frac{\pi}{a}, \tag{VI.46}$$

corresponds to the high frequency modes at the edge of the zone. For $T \gg T_D$, all modes behave classically. The integrand of eq.(VI.45) is just $k_B T$, and since the total number of modes is $3N = 3V \int^{\text{B.Z.}} d^3\vec{k}/(2\pi)^3$, the classical results of $E(T) = E_0 + 3Nk_BT$, and $C = 3Nk_B$ are recovered. For $T \ll T_D$, the factor $\exp(\beta\hbar vk)$ in the denominator of eq.(VI.45) is very large at the Brillouin zone edge. The most important contribution to the integral comes from small k, and the error in extending the integration range to infinity is small. After changing variables to $x = \beta\hbar v|\vec{k}|$, and using $d^3\vec{k} = 4\pi x^2 dx/(\beta\hbar v)^3$ due to spherical symmetry, eq.(VI.45) gives

$$\begin{aligned} \lim_{T \ll T_D} E(T) &\approx E_0 + \frac{3V}{8\pi^3} \left(\frac{k_B T}{\hbar v}\right)^3 4\pi k_B T \int_0^\infty dx \frac{x^3}{e^x - 1} \\ &= E_0 + \frac{\pi^2}{10} V \left(\frac{kT}{\hbar v}\right)^3 k_B T. \end{aligned} \tag{VI.47}$$

(The value of the definite integral, $\pi^4/15 \approx 6.5$, can be found in standard tables.) The resulting heat capacity,

$$C = \frac{dE}{dT} = k_B V \frac{2\pi^2}{5} \left(\frac{k_B T}{\hbar v}\right)^3, \tag{VI.48}$$

has the form $C \propto Nk_B \left(T/T_D\right)^3$ in agreement with observations. The physical interpretation of this result is the following: At temperatures $T \ll T_D$, only a fraction of the phonon modes can be thermally excited. These are the low frequency phonons with energy quanta $\hbar\omega(\vec{k}\,) \ll k_B T$. The excited phonons have wavevectors $|\vec{k}| < k^*(T) \approx (k_B T/\hbar v)$. Quite generally, in d space dimensions, the number of these modes is approximately $Vk^*(T)^d \sim V(k_B T/\hbar v)^d$. Each excited mode can be treated classically, and contributes roughly $k_B T$ to the internal energy which thus scales as $E \sim V(k_B T/\hbar v)^d k_B T$. The corresponding heat capacity, $C \sim Vk_B(k_B T/\hbar v)^d$, vanishes as T^d.

VI.C Black-body Radiation

Phonons correspond to vibrations of a solid medium. There are also (longitudinal) sound modes in liquid and gas states. However, even "empty" vacuum, can support fluctuations of the electromagnetic (EM) field, *photons*, which can be thermally excited at finite temperatures. The normal modes of this field are EM waves, characterized by a wave-number $\vec{k}$, and two possible polarizations α. (Since $\nabla \cdot \vec{E} = 0$ in free space, the electric field must be normal to $\vec{k}$, and only *transverse* modes exist.) With appropriate choice of coordinates, the Hamiltonian for the EM field can be written as a sum of harmonic oscillators,

$$\mathcal{H} = \frac{1}{2} \sum_{\vec{k},\alpha} \left[\left| \tilde{p}_{\vec{k},\alpha} \right|^2 + \omega_\alpha(\vec{k})^2 \left| \tilde{u}_\alpha(\vec{k}) \right|^2 \right], \tag{VI.49}$$

with $\omega_\alpha(\vec{k}) = ck$, where c is the speed of light.

With periodic boundary conditions, the allowed wavevectors in a box of size L are $\vec{k} = 2\pi(n_x, n_y, n_z)/L$ where $\{n_x, n_y, n_z\}$ are integers. However, unlike phonons, there is no Brillouin zone limiting the size of $\vec{k}$, and these integers can be arbitrarily large. The lack of such a restriction leads to the *ultraviolet catastrophe* in a classical treatment: As there is no limit to the wavevector, assigning $k_B T$ per mode leads to an infinite energy stored in the high frequency modes. (The low frequencies are cut off by the finite size of the box.) It was indeed to resolve this difficulty that Planck suggested that the allowed values of EM energy must be quantized according to the Hamiltonian

$$\mathcal{H}^q = \sum_{\vec{k},\alpha} \hbar ck \left(n_\alpha(\vec{k}) + \frac{1}{2} \right), \quad \text{with} \quad n_\alpha(\vec{k}) = 0, 1, 2, \cdots. \tag{VI.50}$$

As for phonons, the internal energy is calculated from

$$E = \langle \mathcal{H}^q \rangle = \sum_{\vec{k},\alpha} \hbar ck \left(\frac{1}{2} + \frac{e^{-\beta\hbar ck}}{1 - e^{-\beta\hbar ck}} \right) = V E_0 + \frac{2V}{(2\pi)^3} \int d^3\vec{k} \frac{\hbar ck}{e^{\beta\hbar ck} - 1}. \tag{VI.51}$$

The zero–point energy is actually infinite, but as only energy differences are measured, it is usually ignored. The change of variables to $x = \beta\hbar ck$ allows us to calculate the excitation energy,

$$\begin{aligned} \frac{E^*}{V} &= \frac{\hbar c}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^4 \int_0^\infty \frac{dx\ x}{e^x - 1} \\ &= \frac{\pi^2}{15} \left(\frac{k_B T}{\hbar c} \right)^3 k_B T. \end{aligned} \tag{VI.52}$$

The EM radiation also exerts a pressure on the walls of the container. From the partition function of the Hamiltonian (VI.50),

$$Z = \sum_{\{n_\alpha(\vec{k})\}} \exp\left[-\beta\hbar\omega(\vec{k})\left(n_\alpha(\vec{k}) + \frac{1}{2}\right)\right] = \prod_{\vec{k},\alpha} \frac{e^{-\beta\hbar ck/2}}{1 - e^{-\beta\hbar ck}}, \tag{VI.53}$$

the free energy is

$$\begin{aligned} F = -k_B T \ln Z &= k_B T \sum_{\vec{k},\alpha} \left[\frac{\beta\hbar ck}{2} + \ln\left(1 - e^{-\beta\hbar ck}\right)\right] \\ &= 2V \int \frac{d^3\vec{k}}{(2\pi)^3} \left[\frac{\hbar ck}{2} + k_B T \ln\left(1 - e^{-\beta\hbar ck}\right)\right]. \end{aligned} \tag{VI.54}$$

The pressure due to the photon gas is

$$\begin{aligned} P &= -\left.\frac{\partial F}{\partial V}\right|_T = -\int \frac{d^3\vec{k}}{(2\pi)^3} \left[\hbar ck + 2k_B T \ln\left(1 - e^{-\beta\hbar ck}\right)\right] \\ &= P_0 - \frac{k_B T}{\pi^2} \int_0^\infty dk\ k^2 \ln\left(1 - e^{-\beta\hbar ck}\right) \quad \text{(integrate by parts)} \\ &= P_0 + \frac{k_B T}{\pi^2} \int_0^\infty dk\ \frac{k^3}{3}\ \frac{\beta\hbar c e^{-\beta\hbar ck}}{1 - e^{-\beta\hbar ck}} \quad \text{(compare with eq.(VI.51))} \\ &= P_0 + \frac{1}{3}\frac{E}{V}\ . \end{aligned} \tag{VI.55}$$

Note that there is also an infinite zero–point pressure P_0. Differences in this pressure lead to the *Casimir force* between conducting plates, which is measurable.

The extra pressure of 1/3 times the energy density can be compared to that of a gas of relativistic particles. (As shown in the test problems, a dispersion relation, $\mathcal{E} \propto |\vec{p}|^s$, leads to a pressure, $P = (s/d)(E/V)$ in d dimensions.) Continuing with the analogy to a gas of particles, if a hole is opened in the container wall, the escaping energy flux per unit area and per unit time is

$$\phi = \langle c_\perp \rangle\ \frac{E}{V}. \tag{VI.56}$$

All photons have speed c, and the average of the component of the velocity perpendicular to the hole can be calculated as

$$\langle c_\perp \rangle = c \times \frac{1}{4\pi} \int_0^{\pi/2} 2\pi \sin\theta d\theta \cos\theta = \frac{c}{4}, \tag{VI.57}$$

resulting in

$$\phi = \frac{1}{4} c \frac{E}{V} = \frac{\pi^2}{60}\ \frac{k_B^4 T^4}{\hbar^3 c^2}. \tag{VI.58}$$

The result, $\phi = \sigma T^4$, is the *Stephan–Boltzmann law* for *blackbody radiation*, and

$$\sigma = \frac{\pi^2}{60}\,\frac{k_B^4}{\hbar^3 c^2} \approx 5.67 \times 10^{-8}\mathrm{Wm}^{-2\circ}\mathrm{K}^{-4}, \tag{VI.59}$$

is *Stephan's constant*. Blackbody radiation has a characteristic frequency dependence: Let $E(T)/V = \int dk \mathcal{E}(k,t)$, where

$$\mathcal{E}(k,T) = \frac{\hbar c}{\pi^2}\,\frac{k^3}{e^{\beta\hbar c k}-1}, \tag{VI.60}$$

is the energy density in wavevector k. The flux of emitted radiation in the interval $[k, k+dk]$ is $I(k,T)dk$, where

$$I(k,T) = \frac{c}{4}\mathcal{E}(k,T) = \frac{\hbar c^2}{4\pi^2}\,\frac{k^3}{e^{\beta\hbar c k}-1} \to \begin{cases} c k_B T k^2/4\pi & \text{for } k \ll k^*(T) \\ \\ \hbar c^2 k^3 e^{-\beta\hbar c k}/4\pi^2 & \text{for } k \gg k^*(T) \end{cases} . \tag{VI.61}$$

The characteristic wavevector $k^*(T) \approx k_B T/\hbar c$ separates quantum and classical regimes. It provides the upper cutoff that eliminates the ultraviolet catastrophe.

VI.D Quantum microstates

In the previous sections we indicated several failures of classical statistical mechanics, which were heuristically remedied by assuming quantized energy levels, while still calculating thermodynamic quantities from a partition sum $Z = \sum_n \exp(-\beta E_n)$. This implicitly assumes that the micro-states of a quantum system are specified by its discretized energy levels, and governed by a probability distribution similar to a Boltzmann weight. This 'analogy' to classical statistical mechanics needs to be justified. Furthermore, quantum mechanics is itself inherently probabilistic, with uncertainties unrelated to those that lead to probabilities in statistical mechanics. Here, we shall construct a quantum formulation of statistical mechanics by closely following the steps that lead to the classical formulation.

Micro-states of a classical system of particles are described by the set of coordinates and conjugate momenta $\{\vec{p}_i, \vec{q}_i\}$; i.e. by a point in the $6N$–dimensional phase space. In quantum mechanics $\{\vec{q}_i\}$ and $\{\vec{p}_i\}$ are not independent observables. Instead:

• The (micro-) state of a quantum system is completely specified by a *unit vector* $|\Psi\rangle$, which belongs to an infinite dimensional *Hilbert space*. The vector $|\Psi\rangle$ can be written in terms of its components $\langle n|\Psi\rangle$, which are complex numbers, along a suitable set of ortho-normal basis vectors $|n\rangle$. In the convenient notation introduced by Dirac, this decomposition is written as

$$|\Psi\rangle = \sum_n \langle n|\Psi\rangle \ |n\rangle. \tag{VI.62}$$

The most familiar basis is that of coordinates $|\{\vec{q}_i\}\rangle$, and $\langle\{\vec{q}_i\}|\Psi\rangle \equiv \Psi(\vec{q}_1, \ldots, \vec{q}_N)$ is the *wave-function*. The normalization condition is

$$\langle\Psi|\Psi\rangle \ = \sum_n \langle\Psi|n\rangle \ \langle n|\Psi\rangle = 1, \quad \text{where} \quad \langle\Psi|n\rangle \ \equiv \langle n|\Psi\rangle^*. \tag{VI.63}$$

For example, in the coordinate basis, we must require

$$\langle\Psi|\Psi\rangle \ = \int \prod_{i=1}^{N} d^d\vec{q}_i \, |\Psi(\vec{q}_1, \ldots, \vec{q}_N)|^2 = 1. \tag{VI.64}$$

• Classically, various observables are functions $\mathcal{O}(\{\vec{p}_i, \vec{q}_i\})$, defined in phase space. In quantum mechanics, these functions are replaced by *Hermitian matrices* (operators) in Hilbert space, obtained by substituting operators for $\{\vec{q}_i\}$ and $\{\vec{p}_i\}$ in the classical expression (after proper symmetrization of products, e.g. $pq \to (pq + qp)/2$). These basic operators satisfy the *commutation* relations,

$$[\, p_j, q_k \,] \equiv p_j q_k - q_k p_j = \frac{\hbar}{i} \, \delta_{j,k} \ . \tag{VI.65}$$

For example, in the coordinate basis $|\{\vec{q}_i\}\rangle$, the momentum operators are

$$p_j = \frac{\hbar}{i}\frac{\partial}{\partial q_j}. \tag{VI.66}$$

(Note that classical Poisson brackets satisfy $\{p_j, q_k\} = -\delta_{j,k}$. Quite generally, quantum commutation relations are obtained by multiplying the corresponding classical Poisson brackets by $i\hbar$.)

• Unlike in classical mechanics, the value of an operator $\mathcal{O}$ is not uniquely determined for a particular micro-state. It is instead a random variable, whose *average* in a state $|\Psi\rangle$ is given by

$$\langle\mathcal{O}\rangle \equiv \langle\Psi|\mathcal{O}|\Psi\rangle \equiv \sum_{m,n}\langle\Psi|m\rangle\langle m|\mathcal{O}|n\rangle\langle n|\Psi\rangle. \tag{VI.67}$$

For example,

$$\langle U(\{\vec{q}\})\rangle = \int\prod_{i=1}^{N} d^3\vec{q}_i\,\Psi^* U(\{\vec{q}\})\Psi, \quad \text{and,}$$
$$\langle K(\{\vec{p}\})\rangle = \int\prod_{i=1}^{N} d^3\vec{q}_i\,\Psi^* K\left(\left\{\frac{\hbar}{i}\frac{d}{d\vec{q}}\right\}\right)\Psi.$$

To ensure that the expectation value $\langle\mathcal{O}\rangle$ is real, the operators $\mathcal{O}$ must be *Hermitian*, i.e. satisfy

$$\mathcal{O}^\dagger = \mathcal{O}, \quad \text{where} \quad \langle m|\mathcal{O}^\dagger|n\rangle \equiv \langle n|\mathcal{O}|m\rangle^*. \tag{VI.68}$$

When replacing $\vec{p}$ and $\vec{q}$ in a classical operator $\mathcal{O}(\{\vec{p}_i, \vec{q}_i\})$ by corresponding matrices, proper symmetrization of various products is necessary to ensure the above Hermiticity.

Time evolution of micro-states is governed by the Hamiltonian $\mathcal{H}(\{\vec{p}_i, \vec{q}_i\})$. A classical microstate evolves according to Hamilton's equations of motion, while in quantum mechanics the state vector changes in time according to

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \mathcal{H}|\Psi(t)\rangle. \tag{VI.69}$$

A convenient basis is one that *diagonalizes* the matrix $\mathcal{H}$. The energy *eigen-states* satisfy $\mathcal{H}|n\rangle = \mathcal{E}_n|n\rangle$, where $\mathcal{E}_n$ are the *eigen-energies*. Substituting $|\Psi(t)\rangle = \sum_n\langle n|\Psi(t)\rangle|n\rangle$ in eq.(VI.69), and taking advantage of the ortho-normality condition $\langle m|n\rangle = \delta_{m,n}$, yields

$$i\hbar\frac{d}{dt}\langle n|\Psi(t)\rangle = \mathcal{E}_n\langle n|\Psi(t)\rangle, \qquad \Longrightarrow \qquad \langle n|\Psi(t)\rangle = \exp\left(-\frac{i\mathcal{E}_n t}{\hbar}\right)\langle n|\Psi(0)\rangle. \tag{VI.70}$$

The quantum states at two different times can be related by a *time evolution* operator, as

$$|\Psi(t)\rangle = U(t,t_0)|\Psi(t_0)\rangle, \tag{VI.71}$$

which satisfies $i\hbar\partial_t U(t,t_0) = \mathcal{H}U(t,t_0)$, with the boundary condition $U(t_0,t_0) = 1$. *If* $\mathcal{H}$ *is independent of* t, we can solve these equations to yield

$$U(t,t_0) = \exp\left[-\frac{i}{\hbar}\mathcal{H}(t-t_0)\right]. \tag{VI.72}$$

VI.E Quantum macrostates

Macro-states of the system depend on only a few thermodynamic functions. We can form an *ensemble* of a large number $\mathcal{N}$, of micro-states μ_α, corresponding to a given macro-state. The different micro-states occur with probabilities p_α. (For example $p_\alpha = 1/\mathcal{N}$ in the absence of any other information.) When we no longer have exact knowledge of the microstate, it is said to be in a *mixed state*.

Classically, ensemble averages are calculated from

$$\overline{\mathcal{O}(\{\vec{p}_i,\vec{q}_i\})_t} = \sum_\alpha p_\alpha \mathcal{O}\big(\mu_\alpha(t)\big) = \int \prod_{i=1}^{N} d^3\vec{p}_i d^3\vec{q}_i \mathcal{O}\left(\{\vec{p}_i,\vec{q}_i\}\right)\rho\left(\{\vec{p}_i,\vec{q}_i\},t\right), \tag{VI.73}$$

where

$$\rho\left(\{\vec{p}_i,\vec{q}_i\},t\right) = \sum_\alpha p_\alpha \prod_{i=1}^{N} \delta^3\left(\vec{q}_i - \vec{q}_i(t)_\alpha\right)\delta^3\left(\vec{p}_i - \vec{p}_i(t)_\alpha\right), \tag{VI.74}$$

is the *ensemble density*.

Similarly, a mixed quantum state is obtained from a set of possible states $\{|\psi_\alpha\rangle\}$, with probabilities $\{p_\alpha\}$. The ensemble average of the quantum mechanical expectation value in eq.(VI.67) is then given by

$$\begin{aligned}\overline{\langle\mathcal{O}\rangle} &= \sum_\alpha p_\alpha \langle\Psi_\alpha|\mathcal{O}|\Psi_\alpha\rangle = \sum_{\alpha,m,n} p_\alpha \langle\Psi_\alpha|m\rangle\langle n|\Psi_\alpha\rangle\langle m|\mathcal{O}|n\rangle \\ &= \sum_{m,n}\langle n|\rho|m\rangle\langle m|\mathcal{O}|n\rangle = \mathrm{tr}(\rho\mathcal{O}),\end{aligned} \tag{VI.75}$$

where we have introduced a basis $\{|n\rangle\}$, and defined the *density matrix*

$$\langle n|\rho(t)|m\rangle \equiv \sum_\alpha p_\alpha \langle n|\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)|m\rangle. \tag{VI.76}$$

Classically, the probability (density) $\rho(t)$ is a function defined on phase space. As all operators in phase space, it is replaced by a matrix in quantum mechanics. Stripped of the choice of basis, the density matrix is

$$\rho(t) = \sum_\alpha p_\alpha |\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)|. \tag{VI.77}$$

Clearly, ρ corresponds to a *pure state* if and only if $\rho^2 = \rho$.

The density matrix satisfies the following properties:

(i) *Normalization:* Since each $|\Psi_\alpha\rangle$ is normalized to unity,

$$\langle 1\rangle = \mathrm{tr}(\rho) = \sum_n \langle n|\rho|n\rangle = \sum_{\alpha,n} p_\alpha |\langle n|\Psi_\alpha\rangle|^2 = \sum_\alpha p_\alpha = 1. \tag{VI.78}$$

(ii) *Hermiticity:* The density matrix is *Hermitian*, i.e. $\rho^\dagger = \rho$, since

$$\langle m|\rho^\dagger|n\rangle = \langle n|\rho|m\rangle^* = \sum_\alpha p_\alpha \langle\Psi_\alpha|m\rangle\langle n|\Psi_\alpha\rangle = \langle n|\rho|m\rangle, \tag{VI.79}$$

ensuring that the averages in eq.(VI.76) are real numbers.

(iii) *Positivity:* For any $|\Phi\rangle$,

$$\langle\Phi|\rho|\Phi\rangle = \sum_\alpha p_\alpha \langle\Phi|\Psi_\alpha\rangle\langle\Psi_\alpha|\Phi\rangle = \sum_\alpha p_\alpha |\langle\Phi|\Psi_\alpha\rangle|^2 \geq 0. \tag{VI.80}$$

Thus ρ is *positive definite*, implying that all its eigenvalues must be positive.

- *Liouville's theorem* governs the time evolution of the classical density as

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} - \{\mathcal{H}, \rho\} = 0. \tag{VI.81}$$

It is most convenient to examine the evolution of the quantum density matrix in the basis of energy eigen-states, where according to eq.(VI.70)

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\langle n|\rho(t)|m\rangle &= i\hbar\frac{\partial}{\partial t}\sum_\alpha p_\alpha \langle n|\Psi_\alpha(t)\rangle\langle\Psi_\alpha(t)|m\rangle \\ &= \sum_\alpha p_\alpha \left[(\mathcal{E}_n - \mathcal{E}_m)\langle n|\Psi_\alpha\rangle\langle\Psi_\alpha|m\rangle\right] \\ &= \langle n|(\mathcal{H}\rho - \rho\mathcal{H})|m\rangle. \end{aligned} \tag{VI.82}$$

The final result is a tensorial identity, and hence, *independent* of the choice of basis

$$i\hbar\frac{\partial}{\partial t}\rho = [\mathcal{H}, \rho]. \tag{VI.83}$$

Equilibrium requires *time independent* averages, and suggests $\partial\rho/\partial t = 0$. This condition is satisfied in both eqs.(VI.81) and (VI.83) by choosing $\rho = \rho(\mathcal{H})$. (As discussed in chapter III, ρ may also depend on conserved quantities such that $[\mathcal{H}, L] = 0$.) Various equilibrium quantum density matrices can now be constructed in analogy to classical statistical mechanics.

• *Microcanonical ensemble:* As the internal energy has a fixed value E, a density matrix that includes this constraint is

$$\rho(E) = \frac{\delta(\mathcal{H} - E)}{\Omega(E)}. \tag{VI.84}$$

In particular, in the basis of energy eigen-states,

$$\langle n|\rho|m\rangle = \sum_\alpha p_\alpha \langle n|\Psi_\alpha\rangle\langle\Psi_\alpha|m\rangle = \begin{cases} \frac{1}{\Omega} & \text{if } \mathcal{E}_n = E, \text{ and } m = n, \\ 0 & \text{if } \mathcal{E}_n \neq E, \text{ or } m \neq n. \end{cases} \tag{VI.85}$$

The first condition states that only eigen-states of the correct energy can appear in the quantum wave-function, and that (for $p_\alpha = 1/\mathcal{N}$) such states on average have the same amplitude, $\overline{|\langle n|\Psi\rangle|^2} = 1/\Omega$. This is equivalent to the classical postulate of equal *a priori* equilibrium probabilities. The second (additional) condition states that the Ω eigen-states of energy E are combined in a typical micro-state with *independent random phases*. (Note that the normalization condition $\mathrm{tr}\,\rho = 1$, implies that $\Omega(E) = \sum_n \delta(E - E_n)$ is the number of eigen-states of $\mathcal{H}$ with energy E.)

• *Canonical ensemble:* A fixed temperature $T = 1/k_B\beta$, can be achieved by putting the system in contact with a reservoir. By considering the combined system, the canonical density matrix is obtained as

$$\rho(\beta) = \frac{\exp(-\beta\mathcal{H})}{Z(\beta)}. \tag{VI.86}$$

The normalization condition $\mathrm{tr}(\rho) = 1$, leads to the quantum partition function

$$Z = \mathrm{tr}\left(e^{-\beta\mathcal{H}}\right) = \sum_n e^{-\beta\mathcal{E}_n}. \tag{VI.87}$$

The final sum is over the (discrete) energy levels of $\mathcal{H}$, and justifies the calculations performed in the previous sections.

• *Grand Canonical Ensemble:* The number of particles N, is no longer fixed. Quantum micro-states with indefinite particle number span a so called *Fock* space. The density matrix is

$$\rho(\beta,\mu) = \frac{e^{-\beta\mathcal{H}+\beta\mu N}}{\mathcal{Q}}, \quad \text{where} \quad \mathcal{Q}(\beta,\mu) = \mathrm{tr}\left(e^{-\beta\mathcal{H}+\beta\mu N}\right) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta). \tag{VI.88}$$

Example: Consider a single particle in a quantum canonical ensemble in a box of volume V. The energy eigen-states of the Hamiltonian

$$\mathcal{H}_1 = \frac{\vec{p}^{\,2}}{2m} = -\frac{\hbar^2}{2m}\nabla^2, \quad \text{(in coordinate basis)} \tag{VI.89}$$

obtained from $\mathcal{H}_1|\vec{k}\,\rangle = \mathcal{E}(\vec{k}\,)|\vec{k}\,\rangle$, are

$$\langle \vec{x}\,|\vec{k}\,\rangle = \frac{e^{i\vec{k}\cdot\vec{x}}}{\sqrt{V}}, \qquad \text{with} \qquad \mathcal{E}(\vec{k}) = \frac{\hbar^2 k^2}{2m}. \tag{VI.90}$$

With periodic boundary conditions in a box of size L, the allowed values of $\vec{k}$ are $(2\pi/L)(\ell_x, \ell_y, \ell_z)$, where (ℓ_x, ℓ_y, ℓ_z) are integers. A particular vector in this one-particle Hilbert space is specified by its components along each of these basis states (infinite in number). The space of quantum micro-states is thus much larger than the corresponding 6-dimensional classical phase space. The partition function for $L \to \infty$,

$$\begin{aligned} Z_1 = \mathrm{tr}(\rho) &= \sum_{\vec{k}} \exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right) = V \int \frac{d^3\vec{k}}{(2\pi)^3} \exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right) \\ &= \frac{V}{(2\pi)^3}\left(\sqrt{\frac{2\pi m k_B T}{\hbar^2}}\right)^3 = \frac{V}{\lambda^3}, \end{aligned} \tag{VI.91}$$

coincides with the classical result, with $\lambda = h/\sqrt{2\pi m k T}$ (justifying the use of $d^3\vec{p}\; d^3\vec{q}/h^3$ as the correct dimensionless measure of phase space). Elements of the density matrix in a coordinate representation are

$$\begin{aligned} \langle \vec{x}\,'|\rho|\vec{x}\,\rangle &= \sum_{\vec{k}} \langle \vec{x}\,'|\vec{k}\,\rangle \frac{e^{-\beta\mathcal{E}(\vec{k}\,)}}{Z_1} \langle \vec{k}\,|\vec{x}\,\rangle = \frac{\lambda^3}{V}\int \frac{V d^3\vec{k}}{(2\pi)^3}\, \frac{e^{-i\vec{k}\cdot(\vec{x}-\vec{x}\,')}}{V} \exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right) \\ &= \frac{1}{V}\exp\left[-\frac{m(\vec{x}-\vec{x}\,')^2}{2\beta\hbar^2}\right] = \frac{1}{V}\exp\left[-\frac{\pi(\vec{x}-\vec{x}\,')^2}{\lambda^2}\right]. \end{aligned} \tag{VI.92}$$

The diagonal elements, $\langle \vec{x}\,|\rho|\vec{x}\,\rangle = 1/V$, are just the probabilities for finding a particle at $\vec{x}$. The off-diagonal elements have no classical analog. They suggest that the appropriate way to think of the particle is as a wave-packet of size $\lambda = h/\sqrt{2\pi m k_B T}$, the *thermal wavelength*. As $T \to \infty$, λ goes to zero, and the classical analysis is valid. As $T \to 0$, λ diverges and quantum mechanical effects take over when λ becomes comparable to the size of the box.

Alternatively, we could have obtained eq.(VI.92), by noting that eq.(VI.86) implies

$$\frac{\partial}{\partial\beta} Z\rho = -\mathcal{H} Z\rho = \frac{\hbar^2}{2m}\nabla^2 Z\rho. \tag{VI.93}$$

This is just the diffusion equation (for the free particle), which can be solved subject to the initial condition $\rho(\beta = 0) = 1$ (i.e. $\langle \vec{x}\,'|\rho(\beta=0)|\vec{x}\,\rangle = \delta^3(\vec{x}-\vec{x}\,')/V$) to yield the result of eq.(VI.92).

VII. Ideal Quantum Gases

VII.A Hilbert Space of Identical Particles

In chapter IV, we discussed the Gibbs paradox for the mixing entropy of gases of identical particles. This difficulty was overcome by postulating that the phase space for N identical particles must be divided by $N!$, the number of permutations. This is not quite satisfactory as the classical equations of motion implicitly treat the particles as distinct. In quantum mechanics, by contrast, the identity of particles appears at the level of allowed states in Hilbert space. For example, the probability of finding two identical particles at positions $\vec{x}_1$ and $\vec{x}_2$ is $|\Psi(\vec{x}_1, \vec{x}_2)|^2$. Since the exchange of particles 1 and 2 leads to the same configurations, we must have $|\Psi(\vec{x}_1, \vec{x}_2)|^2 = |\Psi(\vec{x}_2, \vec{x}_1)|^2$. For a single-valued function, this leads to two possibilities:

$$|\psi(1,2)\rangle = +|\psi(2,1)\rangle, \qquad \text{or} \qquad |\psi(1,2)\rangle = -|\psi(2,1)\rangle \quad . \tag{VII.1}$$

The Hilbert space used to describe identical particles is thus restricted to obey certain symmetries.

For a system of N identical particles, there are $N!$ permutations P, forming a group S_N. There are several ways for representing a permutation; e.g., $P(1\ 2\ 3\ 4) = (3\ 2\ 4\ 1)$ for $N = 4$ can alternatively be indicated by

$$P = \begin{pmatrix} 1 & 2 & 3 & 4 \\ & & & \\ 3 & 2 & 4 & 1 \end{pmatrix}. \tag{VII.2}$$

Any permutation can be obtained from a sequence of two particle exchanges. For example, the above permutation is obtained by the exchanges (1,3) and (1,4) performed in sequence. The *parity* of a permutation is defined as

$$(-1)^P \equiv \begin{cases} +1 & \text{if } P \text{ involves to an } \textit{even} \text{ number of exchanges, e.g. } (1\ 2\ 3) \to (2\ 3\ 1) \\ -1 & \text{if } P \text{ involves an } \textit{odd} \text{ number of exchanges, e.g. } (1\ 2\ 3) \to (2\ 1\ 3) \end{cases} .$$

(Note that if lines are drawn connecting the initial an final locations of each integer in eq.(VII.2), the parity is (-1) raised to the number of intersections of these lines.)

The action of permutations on an N–particle quantum state leads to a *representation* of the permutation group in Hilbert space. Requiring the wave-function to be single valued, and to give equal probabilities under particle exchange, restricts the representation to be

either fully symmetric or anti-symmetric. This allows for two types of identical particles in nature:

(1) **Bosons** correspond to the fully symmetric representation such that

$$P|\psi(1,\cdots,N)\rangle = +|\psi(1,\cdots,N)\rangle.$$

(2) **Fermions** correspond to the fully anti-symmetric representation such that

$$P|\psi(1,\cdots,N)\rangle = (-1)^P|\psi(1,\cdots,N)\rangle.$$

Of course, the Hamiltonian for identical particles must itself be symmetric, i.e. $P\mathcal{H} = \mathcal{H}$. However, for a given $\mathcal{H}$, there are many eigen-states with different symmetries under permutations. To select the correct set of eigen-states, in quantum mechanics the statistics of the particles (bosons or fermions) is specified independently. For example, consider N non-interacting particles in a box of volume V, with a Hamiltonian

$$\mathcal{H} = \sum_{\alpha=1}^{N} \mathcal{H}_\alpha = \sum_{\alpha=1}^{N} \left(-\frac{\hbar^2}{2m}\nabla_\alpha^2 \right). \tag{VII.3}$$

Each $\mathcal{H}_\alpha$ can be separately diagonalized, with plane wave states $\{|\vec{k}\,\rangle\}$ and corresponding energies $\mathcal{E}(\vec{k}\,) = \hbar^2 k^2/2m$. Using sums and products of these one–particle states, we can construct the following–N particle states:

(1) The *product* Hilbert space is obtained by simple multiplication of the one–body states, i.e.

$$|\vec{k}_1,\cdots,\vec{k}_N\rangle_\otimes \equiv |\vec{k}_1\rangle\cdots|\vec{k}_N\rangle. \tag{VII.4}$$

In the coordinate representation,

$$\langle\vec{x}_1,\cdots,\vec{x}_N|\vec{k}_1,\cdots,\vec{k}_N\rangle_\otimes = \frac{1}{V^{N/2}}\exp\left(i\sum_{\alpha=1}^{N}\vec{k}_\alpha\cdot\vec{x}_\alpha \right), \tag{VII.5}$$

and

$$\mathcal{H}|\vec{k}_1,\cdots,\vec{k}_N\rangle_\otimes = \left(\sum_{\alpha=1}^{N}\frac{\hbar^2}{2m}k_\alpha^2 \right)|\vec{k}_1,\cdots,\vec{k}_N\rangle_\otimes. \tag{VII.6}$$

But the product states do not satisfy the symmetry requirements for identical particles, and we must find the appropriate *subspaces* of correct symmetry.

(2) The *fermionic* subspace is constructed as

$$|\vec{k}_1,\cdots,\vec{k}_N\rangle_- = \frac{1}{\sqrt{N_-}}\sum_P (-1)^P P|\vec{k}_1,\cdots,\vec{k}_N\rangle_\otimes, \tag{VII.7}$$

where the sum is over all $N!$ permutations. Clearly, if any one–particle label $\vec{k}$, appears more than once in the above list, the result is zero and there is no anti-symmetrized state. Anti-symmetrization is possible only when all the N values of $\vec{k}_\alpha$ are different. In this case, there are $N!$ terms in the above sum, and $N_- = N!$ is necessary to ensure normalization. For example, a two–particle anti-symmetrized state is

$$|\vec{k}_1,\vec{k}_2\rangle_- = \frac{(|\vec{k}_1,\vec{k}_2\rangle - |\vec{k}_2,\vec{k}_1\rangle)}{\sqrt{2}}.$$

(If not otherwise indicated, $|\ \vec{k}_1,\cdots,\vec{k}_N\rangle$ refers to the product state.)

(3) Similarly, the *bosonic* subspace is constructed as

$$|\vec{k}_1,\cdots,\vec{k}_N\rangle_+ = \frac{1}{\sqrt{N_+}}\sum_P P|\vec{k}_1,\cdots,\vec{k}_N\rangle_\otimes. \tag{VII.8}$$

In this case, there are no restrictions on the allowed values of $\vec{k}$. A particular one–particle state may be repeated $n_{\vec{k}}$ times in the list, with $\sum_{\vec{k}} n_{\vec{k}} = N$. As we shall prove shortly, proper normalization requires $N_+ = N!\prod_{\vec{k}} n_{\vec{k}}!$. For example, a correctly normalized 3–particle bosonic state is constructed from two one–particle states $|\alpha\rangle$, and one one–particle state $|\beta\rangle$ as ($n_\alpha = 2$, $n_\beta = 1$, and $N_+ = 3!2!1! = 12$)

$$\begin{aligned}|\alpha\alpha\beta\rangle_+ &= \frac{1}{\sqrt{12}}\left(|\alpha\rangle|\alpha\rangle|\beta\rangle + |\alpha\rangle|\beta\rangle|\alpha\rangle + |\beta\rangle|\alpha\rangle|\alpha\rangle + |\alpha\rangle|\alpha\rangle|\beta\rangle + |\beta\rangle|\alpha\rangle|\alpha\rangle + |\alpha\rangle|\beta\rangle|\alpha\rangle\right)\\ &= \frac{1}{\sqrt{3}}\left(|\alpha\rangle|\alpha\rangle|\beta\rangle + |\alpha\rangle|\beta\rangle|\alpha\rangle + |\beta\rangle|\alpha\rangle|\alpha\rangle\right).\end{aligned}$$

- It is convenient to discuss bosons and fermions simultaneously by defining

$$|\{\vec{k}\}\rangle_\eta = \frac{1}{\sqrt{N_\eta}}\sum_P \eta^P P|\{\vec{k}\}\rangle, \text{ with } \eta = \begin{cases} +1 & \text{for bosons} \\ -1 & \text{for fermions}\end{cases}. \tag{VII.9}$$

Each state is *uniquely* specified by a set of *occupation numbers* $\left\{n_{\vec{k}}\right\}$, such that $\sum_{\vec{k}} n_{\vec{k}} = N$, and

(1) For fermions, $|\{\vec{k}\}\rangle_- = 0$, unless $n_{\vec{k}} = 0$ or 1, and $N_- = N!\prod_k n_{\vec{k}}! = N!$.

(2) For bosons, any $\vec{k}$ may be repeated $n_{\vec{k}}$ times, and the normalization is calculated from

$$\begin{aligned}{}_+\langle\{\vec{k}\}|\{\vec{k}\}\rangle_+ &= \frac{1}{N_+}\sum_{P,P'}\langle P\{\vec{k}\}|P'\{\vec{k}\}\rangle = \frac{N!}{N_+}\sum_P\langle\{\vec{k}\}|P\{\vec{k}\}\rangle\\ &= \frac{N!\prod_{\vec{k}} n_{\vec{k}}!}{N_+} = 1, \quad \Rightarrow \quad N_+ = N!\prod_k n_{\vec{k}}! \quad .\end{aligned} \tag{VII.10}$$

(The term$\langle\{\vec{k}\}|P\{\vec{k}\}\rangle$ is zero unless the permuted $\vec{k}$'s are identical to the original set, which happens $\prod_{\vec{k}} n_{\vec{k}}!$ times.)

VII.B Canonical Formulation

Using the states constructed in the previous section, we can calculate the canonical density matrix for non-interacting identical particles. In the coordinate representation we have

$$\langle\{\vec{x}\,'\}|\rho|\{\vec{x}\}\rangle_\eta = {\sum_{\{\vec{k}\}}}' \sum_{P,P'} \eta^P \eta^{P'} \langle\{\vec{x}\,'\}|P'\{\vec{k}\}\rangle \rho(\{\vec{k}\}) \langle P\{\vec{k}\}|\{\vec{x}\}\rangle \frac{1}{N_\eta}, \tag{VII.11}$$

where $\rho(\{\vec{k}\}) = \exp\left[-\beta\left(\sum_{\alpha=1}^N \hbar^2 k_\alpha^2/2m\right)\right]/Z_N$. The sum, $\sum'_{\{\vec{k}_1,\vec{k}_2,\cdots,\vec{k}_N\}}$, is restricted to ensure that each identical particle state appears once and only once. In both the bosonic and fermionic subspaces, the set of occupation numbers $\{n_{\vec{k}}\}$ uniquely identify a state. We can, however, remove this restriction from eq.(VII.11), if we divide by the resulting over-counting factor (for bosons) of $N!/(\prod_{\vec{k}} n_{\vec{k}}!)$, i.e.,

$${\sum_{\{\vec{k}\}}}' = \sum_{\{\vec{k}\}} \frac{\prod_{\vec{k}} n_{\vec{k}}!}{N!}.$$

(Note that for fermions, the $(-1)^P$ factors cancel out the contributions from cases where any $n_{\vec{k}}$ is larger than one.) Therefore,

$$\begin{aligned}\langle\{\vec{x}\,'\}|\rho|\{\vec{x}\}\rangle = &\sum_{\{\vec{k}\}} \frac{\prod_{\vec{k}} n_{\vec{k}}!}{N!} \cdot \frac{1}{N! \prod_{\vec{k}} n_{\vec{k}}!} \cdot \\ &\sum_{P,P'} \frac{\eta^P \eta^{P'}}{Z_N} \exp\left(-\beta \sum_{\alpha=1}^N \frac{\hbar^2 k_\alpha^2}{2m}\right) \langle\{\vec{x}\,'\}|P'\{\vec{k}\}\rangle \langle P\{\vec{k}\}|\{\vec{x}\}\rangle.\end{aligned} \tag{VII.12}$$

In the limit of large volume, the sums over $\{\vec{k}\}$ can be replaced by integrals, and using the plane wave representation of wavefunctions, we have

$$\begin{aligned}\langle\{\vec{x}\,'\}|\rho|\{\vec{x}\}\rangle = &\frac{1}{Z_N (N!)^2} \sum_{P,P'} \eta^P \eta^{P'} \int \prod_{\alpha=1}^N \frac{V\, d^3\vec{k}_\alpha}{(2\pi)^3} \exp\left(-\frac{\beta\hbar^2 k_\alpha^2}{2m}\right) \\ &\times \left\{ \frac{\exp\left[-i \sum_{\alpha=1}^N (\vec{k}_{P\alpha} \cdot \vec{x}_\alpha - \vec{k}_{P'\alpha} \cdot \vec{x}\,'_\alpha)\right]}{V^N} \right\}.\end{aligned} \tag{VII.13}$$

We can order the sum in the exponent by focusing on a particular $\vec{k}$-vector. Since $\sum_\alpha f(P\alpha) g(\alpha) = \sum_\beta f(\beta) g(P^{-1}\beta)$, where $\beta = P\alpha$ and $\alpha = P^{-1}\beta$, we obtain

$$\langle\{\vec{x}\,'\}|\rho|\{\vec{x}\}\rangle = \frac{1}{Z_N (N!)^2} \sum_{P,P'} \eta^P \eta^{P'} \prod_{\alpha=1}^N \left[\int \frac{d^3\vec{k}_\alpha}{(2\pi)^3} e^{-i\vec{k}_\alpha \cdot \left(\vec{x}_{P^{-1}\alpha} - \vec{x}\,'_{P'^{-1}\alpha}\right) - \beta\hbar^2 k_\alpha^2/2m} \right]. \tag{VII.14}$$

The gaussian integrals in the square brackets are equal to

$$\frac{1}{\lambda^3}\exp\left[-\frac{\pi}{\lambda^2}\left(\vec{x}_{P^{-1}\alpha}-\vec{x}\,'_{P'^{-1}\alpha}\right)^2\right].$$

Setting $\beta = P^{-1}\alpha$ in eq.(VII.14) gives

$$\langle\{\vec{x}\,'\}|\rho|\{\vec{x}\}\rangle = \frac{1}{Z_N\lambda^{3N}(N!)^2}\sum_{P,P'}\eta^P\eta^{P'}\exp\left[-\frac{\pi}{\lambda^2}\sum_{\beta=1}^{N}\left(\vec{x}_\beta-\vec{x}\,'_{P'^{-1}P\beta}\right)^2\right]. \qquad \text{(VII.15)}$$

Finally, we set $Q = P'^{-1}P$, and use the results $\eta^P = \eta^{P^{-1}}$, and $\eta^Q = \eta^{P'^{-1}P} = \eta^{P'}\eta^P$, to get (after performing $\sum_P = N!$)

$$\langle\{\vec{x}\,'\}|\rho|\{\vec{x}\}\rangle = \frac{1}{Z_N\lambda^{3N}N!}\sum_{Q}\eta^Q\exp\left[-\frac{\pi}{\lambda^2}\sum_{\beta=1}^{N}\left(\vec{x}_\beta-\vec{x}\,'_{Q\beta}\right)^2\right]. \qquad \text{(VII.16)}$$

The canonical partition function, Z_N, is obtained from the normalization condition

$$\mathrm{tr}(\rho)=1, \quad \Longrightarrow \quad \int\prod_{\alpha=1}^{N}d^3\vec{x}_\alpha\ \langle\{\vec{x}\}|\rho|\{\vec{x}\}\rangle = 1,$$

as

$$Z_N = \frac{1}{N!\lambda^{3N}}\int\prod_{\alpha=1}^{N}d^3\vec{x}_\alpha\sum_{Q}\eta^Q\exp\left[-\frac{\pi}{\lambda^2}\sum_{\beta=1}^{N}\left(\vec{x}_\beta-\vec{x}_{Q\beta}\right)^2\right]. \qquad \text{(VII.17)}$$

The quantum partition function thus involves a sum over $N!$ possible permutations. The classical result $Z_N = \left(V/\lambda^3\right)^N/N!$, is obtained from the term corresponding to no particle exchange, $Q \equiv 1$. The division by $N!$ finally justifies the factor that was (somewhat artificially) introduces in classical statistical mechanics to deal with the phase space of identical particles. However, this classical result is only valid at very high temperature and is modified by the quantum corrections coming from the remaining permutations. As any permutation involves a product of factors $\exp[-\pi(\vec{x}_1-\vec{x}_2)^2/\lambda^2]$, its contributions vanishes as $\lambda \to 0$ for $T \to \infty$.

The lowest order correction comes from the simplest permutation which is the exchange of two particles. The exchange of particles 1 and 2 is accompanied by a factor of $\eta\exp[-2\pi(\vec{x}_1-\vec{x}_2)^2/\lambda^2]$. As each of the possible $N(N-1)/2$ pairwise exchanges gives the same contribution to Z_N, we get

$$Z_N = \frac{1}{N!\lambda^{3N}}\int\prod_{\alpha=1}^{N}d^3\vec{x}_\alpha\left\{1+\frac{N(N-1)}{2}\eta\exp\left[-\frac{2\pi}{\lambda^2}(\vec{x}_1-\vec{x}_2)^2\right]+\cdots\right\}. \qquad \text{(VII.18)}$$

For any $\alpha \geq 2$, $\int d^3\vec{x}_\alpha = V$; in the remaining two integrations we can use the relative, $\vec{r}_{12} = \vec{x}_2 - \vec{x}_1$, and center of mass coordinates to get

$$\begin{aligned} Z_N &= \frac{1}{N!\lambda^{3N}} V^N \left[1 + \frac{N(N-1)}{2V} \eta \int d^3\vec{r}_{12}\, e^{-2\pi \vec{r}_{12}^{\,2}/\lambda^2} + \cdots \right] \\ &= \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \left[1 + \frac{N(N-1)}{2V} \cdot \left(\sqrt{\frac{2\pi\lambda^2}{4\pi}} \right)^3 \eta + \cdots \right]. \end{aligned} \tag{VII.19}$$

From the corresponding free energy,

$$F = -k_B T \ln Z_N = -N k_B T \ln \left[\frac{e}{\lambda^3} \cdot \frac{V}{N} \right] - \frac{k_B T N^2}{2V} \cdot \frac{\lambda^3}{2^{3/2}} \eta + \cdots, \tag{VII.20}$$

the gas pressure is computed as

$$P = -\left. \frac{\partial F}{\partial V} \right|_T = \frac{N k_B T}{V} - \frac{N^2 k_B T}{V^2} \cdot \frac{\lambda^3}{2^{5/2}} \eta + \cdots = n k_B T \left[1 - \frac{\eta \lambda^3}{2^{5/2}} n + \cdots \right]. \tag{VII.21}$$

Note that the first quantum correction is equivalent to a second virial coefficient of

$$B_2 = -\frac{\eta \lambda^3}{2^{5/2}}. \tag{VII.22}$$

The resulting correction to pressure is negative for bosons, and positive for fermions. In the classical formulation, a second virial coefficient was obtained from a two-body interaction. The classical potential $\mathcal{V}(\vec{r})$ that leads to the second virial coefficient in eq.(VII.22) is obtained from

$$\begin{aligned} f(\vec{r}) &= e^{-\beta \mathcal{V}(\vec{r})} - 1 = \eta e^{-2\pi \vec{r}^{\,2}/\lambda^2}, \quad \Longrightarrow \\ \mathcal{V}(\vec{r}) &= -k_B T \ln \left[1 + \eta e^{-2\pi \vec{r}^{\,2}/\lambda^2} \right] \approx -k_B T \eta\, e^{-2\pi \vec{r}^{\,2}/\lambda^2}. \end{aligned} \tag{VII.23}$$

(The final approximation corresponds to high temperatures, where only the first correction is important). Thus the effects of quantum statistics at high temperatures are approximately equivalent to introducing an interaction between particles. The interaction is attractive for bosons, repulsive for fermions, and operates over distances of the order of the thermal wavelength λ.

VII.C Grand Canonical Formulation

Calculating the partition function by performing all the sums in eq.(VII.17) is a formidable task. Alternatively, we can compute Z_N in the energy basis as

$$Z_N = \mathrm{tr}\,\left(e^{-\beta\mathcal{H}}\right) = \sum_{\{\vec{k}_\alpha\}}{}' \exp\left[-\beta\sum_{\alpha=1}^{N}\mathcal{E}(\vec{k}_\alpha)\right] = \sum_{\{n_{\vec{k}}\}}{}' \exp\left[-\beta\sum_{\vec{k}}\mathcal{E}(\vec{k})n(\vec{k})\right]. \quad \text{(VII.24)}$$

These sums are still difficult to perform due to the restrictions of symmetry on the allowed values of $\vec{k}$ or $\{n_{\vec{k}}\}$: The occupation numbers $\{n_{\vec{k}}\}$ are restricted to $\sum_{\vec{k}} n_{\vec{k}} = N$, and $n_{\vec{k}} = 0, 1, 2, \cdots$ for bosons, while $n_{\vec{k}} = 0$ or 1 for fermions. As usual, the first constraint can be removed by looking at the grand partition function,

$$\begin{aligned}\mathcal{Q}_\eta(T,\mu) &= \sum_{N=0}^{\infty} e^{\beta\mu N}\sum_{\{n_{\vec{k}}\}}{}' \exp\left[-\beta\sum_{\vec{k}}\mathcal{E}(\vec{k})n_{\vec{k}}\right] \\ &= \sum_{\{n_{\vec{k}}\}}^{\eta}\prod_{\vec{k}}\exp\left[-\beta\big(\mathcal{E}(\vec{k})-\mu\big)n_{\vec{k}}\right].\end{aligned} \quad \text{(VII.25)}$$

The sums over $\{n_{\vec{k}}\}$ can now be performed independently for each $\vec{k}$, subject to the restrictions on occupation numbers imposed by particle symmetry.

- For *fermions*, $n_{\vec{k}} = 0$ or 1, and

$$\mathcal{Q}_- = \prod_{\vec{k}}\left[1+\exp\left(\beta\mu-\beta\mathcal{E}(\vec{k})\right)\right]. \quad \text{(VII.26)}$$

- For *bosons*, $n_{\vec{k}} = 0, 1, 2, \cdots$, and summing the geometric series gives

$$\mathcal{Q}_+ = \prod_{\vec{k}}\left[1-\exp\left(\beta\mu-\beta\mathcal{E}(\vec{k})\right)\right]^{-1}. \quad \text{(VII.27)}$$

The results for both cases can be presented simultaneously as

$$\ln\mathcal{Q}_\eta = -\eta\sum_{\vec{k}}\ln\left[1-\eta\exp\left(\beta\mu-\beta\mathcal{E}(\vec{k})\right)\right], \quad \text{(VII.28)}$$

with $\eta = -1$ for fermions, and $\eta = +1$ for bosons.

In the grand canonical formulation, different one-particle states are occupied independently, with a joint probability

$$p_\eta\left(\left\{n(\vec{k})\right\}\right) = \frac{1}{\mathcal{Q}_\eta}\prod_{\vec{k}}\exp\left[-\beta\big(\mathcal{E}(\vec{k})-\mu\big)n_{\vec{k}}\right]. \quad \text{(VII.29)}$$

The *average occupation number* of a state of energy $\mathcal{E}(\vec{k})$ is given by

$$\langle n_{\vec{k}}\rangle_\eta = -\frac{\partial \ln \mathcal{Q}_\eta}{\partial\big(\beta\mathcal{E}(\vec{k})\big)} = \frac{1}{z^{-1}e^{\beta\mathcal{E}(\vec{k})}-\eta}, \tag{VII.30}$$

where $z = \exp(\beta\mu)$. The average values of the particle number and internal energy are then given by

$$\begin{cases} N_\eta = \displaystyle\sum_{\vec{k}} \langle n_{\vec{k}}\rangle_\eta = \sum_{\vec{k}} \frac{1}{z^{-1}e^{\beta\mathcal{E}(\vec{k})}-\eta} \\ E_\eta = \displaystyle\sum_{\vec{k}} \mathcal{E}(\vec{k})\langle n_{\vec{k}}\rangle_\eta = \sum_{\vec{k}} \frac{\mathcal{E}(\vec{k})}{z^{-1}e^{\beta\mathcal{E}(\vec{k})}-\eta} \end{cases}. \tag{VII.31}$$

VII.D Non-relativistic Gas

Quantum particles are further characterized by a *spin* s. In the absence of a magnetic field different spin states have the same energy, and a *spin degeneracy* factor, $g = 2s+1$, multiplies eqs.(VII.28)–(VII.31). In particular, for a non-relativistic gas in three dimensions ($\mathcal{E}(\vec{k}) = \hbar^2k^2/2m$, and $\sum_{\vec{k}} \to V\int d^3\vec{k}/(2\pi)^3$) these equations reduce to

$$\begin{cases} \beta P_\eta = \dfrac{\ln \mathcal{Q}_\eta}{V} = \eta g \displaystyle\int \frac{d^3\vec{k}}{(2\pi)^3}\, \ln\left[1-\eta z\exp\left(-\frac{\beta\hbar^2k^2}{2m}\right)\right], \\ n_\eta \equiv \dfrac{N_\eta}{V} = g\displaystyle\int \frac{d^3\vec{k}}{(2\pi)^3}\, \frac{1}{z^{-1}\exp\left(\frac{\beta\hbar^2k^2}{2m}\right)-\eta}, \\ \varepsilon_\eta \equiv \dfrac{E_\eta}{V} = g\displaystyle\int \frac{d^3\vec{k}}{(2\pi)^3}\, \frac{\hbar^2k^2}{2m}\, \frac{1}{z^{-1}\exp\left(\frac{\beta\hbar^2k^2}{2m}\right)-\eta}. \end{cases} \tag{VII.32}$$

To simplify these equations, we change variables to $x = \beta\hbar^2k^2/(2m)$, so that

$$k = \frac{\sqrt{2mk_BT}}{\hbar}x^{1/2} = \frac{2\pi^{1/2}}{\lambda}x^{1/2}, \qquad \Longrightarrow \qquad dk = \frac{\pi^{1/2}}{\lambda}x^{-1/2}dx.$$

Substituting into eqs.(VII.32) gives

$$\begin{cases} \beta P_\eta = -\eta\, \dfrac{g}{2\pi^2}\, \dfrac{4\pi^{3/2}}{\lambda^3} \displaystyle\int_0^\infty dx\, x^{1/2} \ln\left(1-\eta z e^{-x}\right) \\ \qquad\quad = \dfrac{g}{\lambda^3}\, \dfrac{4}{3\sqrt{\pi}} \displaystyle\int_0^\infty \frac{dx\, x^{3/2}}{z^{-1}e^x-\eta}, \quad \text{(integration by parts)} \\ n_\eta = \dfrac{g}{\lambda^3}\, \dfrac{2}{\sqrt{\pi}} \displaystyle\int_0^\infty \frac{dx\, x^{1/2}}{z^{-1}e^x-\eta}, \\ \beta\varepsilon_\eta = \dfrac{g}{\lambda^3}\, \dfrac{2}{\sqrt{\pi}} \displaystyle\int_0^\infty \frac{dx\, x^{3/2}}{z^{-1}e^x-\eta}\ . \end{cases} \tag{VII.33}$$

We now define two sets of functions by

$$f_m^\eta(z) = \frac{1}{(m-1)!}\int_0^\infty \frac{dx\, x^{m-1}}{z^{-1}e^x - \eta}. \tag{VII.34}$$

For non-integer arguments, the function $m! \equiv \Gamma(m+1)$ is defined by the integral $\int_0^\infty dx\, x^m e^{-x}$. In particular, from this definition it follows that $(1/2)! = \sqrt{\pi}/2$, and $(3/2)! = (3/2)\sqrt{\pi}/2$. Eqs.(VII.33) now take the simple form

$$\begin{cases} \beta P_\eta = \dfrac{g}{\lambda^3} f_{5/2}^\eta(z), \\ n_\eta = \dfrac{g}{\lambda^3} f_{3/2}^\eta(z), \\ \varepsilon_\eta = \dfrac{3}{2} P_\eta \quad . \end{cases} \tag{VII.35}$$

These results completely describe the thermodynamics of ideal quantum gases as a function of z. To find the equation of state $P_\eta(n_\eta, T)$, we need to solve for z in terms of density. This requires knowledge of the behavior of the functions $f_m^\eta(z)$.

The high temperature, low density (non-degenerate) limit will be examined first. In this limit, z is small, and

$$\begin{aligned} f_m^\eta(z) &= \frac{1}{(m-1)!}\int_0^\infty \frac{dx\, x^{m-1}}{z^{-1}e^x - \eta} = \frac{1}{(m-1)!}\int_0^\infty dx\, x^{m-1}\left(ze^{-x}\right)\left(1-\eta z e^{-x}\right)^{-1} \\ &= \frac{1}{(m-1)!}\int_0^\infty dx\, x^{m-1}\sum_{\alpha=1}^\infty \left(ze^{-x}\right)^\alpha\ \eta^{\alpha+1} \\ &= \sum_{\alpha=1}^\infty \eta^{\alpha+1} z^\alpha \frac{1}{(m-1)!}\int_0^\infty dx\, x^{m-1} e^{-\alpha x} \\ &= \sum_{\alpha=1}^\infty \eta^{\alpha+1}\frac{z^\alpha}{\alpha^m} = z + \eta\frac{z^2}{2^m} + \frac{z^3}{3^m} + \eta\frac{z^4}{4^m} + \cdots. \end{aligned} \tag{VII.36}$$

We thus find (self-consistently) that $f_m^\eta(z)$, and hence $n_\eta(z)$ and $P_\eta(z)$, are indeed small as $z \to 0$. Eqs.(VII.35) in this limit give,

$$\begin{cases} \dfrac{n_\eta \lambda^3}{g} = f_{3/2}^\eta(z) = z + \eta\dfrac{z^2}{2^{3/2}} + \dfrac{z^3}{3^{3/2}} + \eta\dfrac{z^4}{4^{3/2}} + \cdots, \\ \dfrac{\beta P_\eta \lambda^3}{g} = f_{5/2}^\eta(z) = z + \eta\dfrac{z^2}{2^{5/2}} + \dfrac{z^3}{3^{5/2}} + \eta\dfrac{z^4}{4^{5/2}} + \cdots. \end{cases} \tag{VII.37}$$

The first of the above equations can be solved perturbatively, by the recursive procedure of substituting the solution up to a lower order, as

$$\begin{aligned} z &= \frac{n_\eta \lambda^3}{g} - \eta \frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} - \cdots \\ &= \left(\frac{n_\eta \lambda^3}{g}\right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2 - \cdots \\ &= \left(\frac{n_\eta \lambda^3}{g}\right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) \left(\frac{n_\eta \lambda^3}{g}\right)^3 - \cdots . \end{aligned} \tag{VII.38}$$

Substituting this solution into the second leads to

$$\begin{aligned} \frac{\beta P_\eta \lambda^3}{g} = \left(\frac{n_\eta \lambda^3}{g}\right) &- \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) \left(\frac{n_\eta \lambda^3}{g}\right)^3 \\ &+ \frac{\eta}{2^{5/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^2 - \frac{1}{8} \left(\frac{n_\eta \lambda^3}{g}\right)^3 + \frac{1}{3^{5/2}} \left(\frac{n_\eta \lambda^3}{g}\right)^3 + \cdots . \end{aligned}$$

The pressure of the quantum gas can thus be obtained from the virial expansion,

$$P_\eta = n_\eta k_B T \left[1 - \frac{\eta}{2^{5/2}} \left(\frac{n_\eta \lambda^3}{g}\right) + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right) \left(\frac{n_\eta \lambda^3}{g}\right)^2 + \cdots\right]. \tag{VII.39}$$

The second virial coefficient $B_2 = -\eta \lambda^3/(2^{5/2} g)$, agrees with eq.(VII.22) computed in the canonical ensemble for $g = 1$. The natural (dimensionless) expansion parameter is $n_\eta \lambda^3/g$, and quantum mechanical effects become important when $n_\eta \lambda^3 \geq g$; the *quantum degenerate* limit. The behavior of fermi and bose gases is very different in this degenerate limit of low temperatures and high densities, and the two cases will be discussed separately in the following sections.

VII.E The Degenerate Fermi Gas

At zero temperature, the fermi occupation number,

$$\langle n_{\vec{k}} \rangle_- = \frac{1}{e^{\beta\left(\mathcal{E}(k)-\mu\right)}+1}, \tag{VII.40}$$

is one for $\mathcal{E}(\vec{k}) < \mu$, and zero otherwise. The limiting value of μ at zero temperature is called the *fermi energy*, $\mathcal{E}_F$, and all one-particle states of energy less than $\mathcal{E}_F$ are occupied, forming a *fermi sea*. For the ideal gas with $\mathcal{E}(\vec{k}) = \hbar^2 k^2/(2m)$, there is a corresponding *fermi wavenumber* k_F, calculated from

$$N = \sum_{|\vec{k}|\leq k_F} (2s+1) = gV \int^{k<k_F} \frac{d^3\vec{k}}{(2\pi)^3} = g\frac{V}{6\pi^2}k_F^3. \tag{VII.41}$$

In terms of the density $n = N/V$,

$$k_F = \left(\frac{6\pi^2 n}{g}\right)^{1/3}, \qquad \Longrightarrow \qquad \mathcal{E}_F(n) = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{g}\right)^{2/3}. \tag{VII.42}$$

Note that while in a classical treatment the ideal gas has a large density of states at $T = 0$ (from $\Omega_{\rm Classical} = V^N/N!$), the quantum fermi gas has a unique ground state with $\Omega = 1$. Once the one-particle momenta are specified (all $\vec{k}$ for $|\vec{k}| < k_F$), there is only one anti-symmetrized state, as constructed in eq.(VII.7).

To see how the fermi sea is modified at small temperatures, we need the behavior of $f_m^-(z)$ for large z which, after integration by parts, is

$$f_m^-(z) = \frac{1}{m!}\int_0^\infty dx\, x^m \frac{d}{dx}\left(\frac{-1}{z^{-1}e^x+1}\right).$$

Since the fermi occupation number changes abruptly from one to zero, its derivative in the above equation is sharply peaked. We can expand around this peak by setting $x = \ln z + t$, and extending the range of integration to $-\infty < t < +\infty$, as

$$\begin{aligned} f_m^-(z) &\approx \frac{1}{m!}\int_{-\infty}^\infty dt\, (\ln z + t)^m \frac{d}{dt}\left(\frac{-1}{e^t+1}\right) \\ &= \frac{1}{m!}\int_{-\infty}^\infty dt \sum_{\alpha=0}^\infty \binom{m}{\alpha} t^\alpha (\ln z)^{m-\alpha} \frac{d}{dt}\left(\frac{-1}{e^t+1}\right) \\ &= \frac{(\ln z)^m}{m!}\sum_{\alpha=0}^\infty \frac{m!}{\alpha!(m-\alpha)!}(\ln z)^{-\alpha}\int_{-\infty}^\infty dt\, t^\alpha \frac{d}{dt}\left(\frac{-1}{e^t+1}\right). \end{aligned} \tag{VII.43}$$

Using the (anti-) symmetry of the integrand under $t \to -t$, and un-doing the integration by parts yields,

$$\frac{1}{\alpha!}\int_{-\infty}^{\infty} dt\; t^{\alpha}\frac{d}{dt}\left(\frac{-1}{e^t+1}\right) = \begin{cases} 0 & \text{for } \alpha \text{ odd,} \\ \dfrac{2}{(\alpha-1)!}\displaystyle\int_0^{\infty} dt\,\frac{t^{\alpha-1}}{e^t+1} = 2f_{\alpha}^{-}(1) & \text{for } \alpha \text{ even.} \end{cases}$$

Inserting the above into eq.(VII.43), and using tabulated values for the integrals $f_{\alpha}^{-}(1)$, leads to the *Sommerfeld expansion*,

$$\begin{aligned}\lim_{z\to\infty} f_m^{-}(z) =& \frac{(\ln z)^m}{m!}\sum_{\alpha=0}^{\text{even}} 2f_{\alpha}^{-}(1)\;\frac{m!}{(m-\alpha)!}\;(\ln z)^{-\alpha} \\ =& \frac{(\ln z)^m}{m!}\left[1+\frac{\pi^2}{6}\;\frac{m(m-1)}{(\ln z)^2}+\frac{7\pi^4}{360}\;\frac{m(m-1)(m-2)(m-3)}{(\ln z)^4}+\cdots\right].\end{aligned} \tag{VII.44}$$

In the degenerate limit, the density and chemical potential are related by

$$\frac{n\lambda^3}{g} = f_{3/2}^{-}(z) = \frac{(\ln z)^{3/2}}{(3/2)!}\left[1+\frac{\pi^2}{6}\;\frac{3}{2}\;\frac{1}{2}\;(\ln z)^{-2}+\cdots\right] \gg 1. \tag{VII.45}$$

The lowest order result reproduces the expression in eq.(VII.41) for the fermi energy,

$$\lim_{T\to 0}\ln z = \left[\frac{3}{4\sqrt{\pi}}\;\frac{n\lambda^3}{g}\right]^{2/3} = \frac{\beta\hbar^2}{2m}\left(\frac{6\pi^2 n}{g}\right)^{2/3} = \beta\mathcal{E}_F.$$

Inserting the zero temperature limit into eq.(VII.45) gives the first order correction,

$$\ln z = \beta\mathcal{E}_F\left[1+\frac{\pi^2}{8}\;\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\cdots\right]^{-2/3} = \beta\mathcal{E}_F\left[1-\frac{\pi^2}{12}\;\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\cdots\right]. \tag{VII.46}$$

The appropriate dimensionless expansion parameter is $(k_BT/\mathcal{E}_F)$. Note that the fermion chemical potential $\mu = k_BT\ln z$, is positive at low temperatures, and negative at high temperatures (from eq.(VII.38)). It changes sign at a temperature proportional to $\mathcal{E}_F/k_B$.

The low temperature expansion for the pressure is

$$\begin{aligned}\beta P =& \frac{g}{\lambda^3}f_{5/2}^{-}(z) = \frac{g}{\lambda^3}\frac{(\ln z)^{5/2}}{(5/2)!}\left[1+\frac{\pi^2}{6}\;\frac{5}{2}\;\frac{3}{2}\;(\ln z)^{-2}+\cdots\right] \\ =& \frac{g}{\lambda^3}\frac{8(\beta\mathcal{E}_F)^{5/2}}{15\sqrt{\pi}}\left[1-\frac{5}{2}\;\frac{\pi^2}{12}\;\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\cdots\right]\left[1+\frac{5\pi^2}{8}\;\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\cdots\right] \\ =& P_F\left[1+\frac{5}{12}\,\pi^2\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\cdots\right],\end{aligned} \tag{VII.47}$$

where $P_F = (2/5)n\mathcal{E}_F$ if the *fermi pressure*. Unlike its classical counterpart, the fermi gas at zero temperature has finite pressure and internal energy.

The low temperature expansion for the internal energy is obtained easily from eq.(VII.47) using

$$\frac{E}{V} = \frac{3}{2}P = \frac{3}{5}nk_BT_F\left[1 + \frac{5}{12}\pi^2\left(\frac{T}{T_F}\right)^2 + \cdots\right], \tag{VII.48}$$

where we have introduced the *fermi temperature* $T_F = \mathcal{E}_F/k_B$. Eq.(VII.48) leads to a low temperature heat capacity,

$$C_V = \frac{dE}{dT} = \frac{\pi^2}{2}Nk_B\left(\frac{T}{T_F}\right) + \mathcal{O}\left(\frac{T}{T_F}\right)^2. \tag{VII.49}$$

The linear vanishing of the heat capacity as $T \to 0$ is a general feature of a fermi gas, valid in all dimensions. It has the following simple physical interpretation: The probability of occupying single-particle states, eq.(VII.40), is very close to a step function at small temperatures. Only particles within a distance of approximately k_BT of the fermi energy can be thermally excited. This represents only a small fraction T/T_F, of the total number of electrons. Each excited particle gains an energy of the order of k_BT, leading to a change in the internal energy of approximately $k_BTN(T/T_F)$. Hence the heat capacity is given by $C_V = dE/dT \sim Nk_BT/T_F$. This conclusion is also valid for an interacting fermi gas. The fact that only a small number, $N(T/T_F)$, of fermions are excited at small temperatures accounts for many interesting properties of fermi gases. For example, the magnetic susceptibility of a classical gas of N non-interacting particles of magnetic moment μ_B follows the Curie law, $\chi \propto N\mu_B^2/(k_BT)$. Since quantum mechanically, only a fraction of spins contributes at low temperatures, the low temperature susceptibility saturates to a (Pauli) value of $\chi \propto N\mu_B^2/(k_BT_F)$. (See review problems for the details of this calculation.)

VII.F The Degenerate Bose Gas

The average boson occupation number,

$$\langle n_{\vec{k}} \rangle_+ = \frac{1}{\exp\left[\beta\left(\mathcal{E}(\vec{k}) - \mu\right)\right] - 1}, \tag{VII.50}$$

must be always positive. This requires $\mathcal{E}(\vec{k}) - \mu$ to be positive for all $\vec{k}$, and hence $\mu < \min\left[\mathcal{E}(\vec{k})\right]_{\vec{k}} = 0$ (for $\mathcal{E}(\vec{k}) = \hbar^2 k^2/2m$). At high temperatures (classical limit), μ is large and *negative*, and increases towards zero as $-k_B T \ln(n\lambda^3/g)$ as temperature is reduced. In the degenerate quantum limit, μ approaches its limiting value of zero. To see how this limit is achieved, and to find out about the behavior of the degenerate bose gas, we have to examine the limiting behavior of the functions $f_m^+(z)$ in eqs.(VII.35) as $z = \exp(\beta\mu)$ goes to unity.

The functions $f_m^+(z)$ are monotonically increasing with z in the interval $0 \leq z \leq 1$. The maximum value attained at $z = 1$ is

$$\zeta_m \equiv f_m^+(1) = \frac{1}{(m-1)!}\int_0^\infty \frac{dx\ x^{m-1}}{e^x - 1}. \tag{VII.51}$$

The integrand has a pole as $x \to 0$, where it behaves as $\int dx x^{m-2}$. Therefore, ζ_m is finite for $m > 1$ and infinite for $m < 1$. A useful recursive property of these functions is (for $m > 1$)

$$\begin{aligned}
\frac{d}{dz} f_m^+(z) &= \int_0^\infty dx\ \frac{x^{m-1}}{(m-1)!}\frac{d}{dz}\left(\frac{1}{z^{-1}e^x - 1}\right) \\
&\qquad \left(\text{use} \quad \frac{d}{dz} f\left(z^{-1}e^x\right) = -\frac{e^x}{z^2} f' = -\frac{1}{z}\frac{d}{dx} f\left(z^{-1}e^x\right)\right) \\
&= -\frac{1}{z}\int_0^\infty dx\ \frac{x^{m-1}}{(m-1)!}\frac{d}{dx}\left(\frac{1}{z^{-1}e^x - 1}\right) \quad \text{(integrate by parts)} \\
&= \frac{1}{z}\int_0^\infty dx\ \frac{x^{m-2}}{(m-2)!}\frac{1}{z^{-1}e^x - 1} = \frac{1}{z} f_{m-1}^+(z).
\end{aligned} \tag{VII.52}$$

Hence, a sufficiently high derivative of $f_m^+(z)$ will be divergent at $z = 1$ for all m.

The density of *excited states* for the non-relativistic bose gas in three dimensions is thus bounded by

$$n_\times = \frac{g}{\lambda^3} f_{3/2}^+(z) \leq n^* = \frac{g}{\lambda^3}\zeta_{3/2}. \tag{VII.53}$$

At sufficiently high temperatures, such that

$$\frac{n\lambda^3}{g} = \frac{n}{g}\left(\frac{h}{\sqrt{2\pi m k_B T}}\right)^3 \leq \zeta_{3/2} \approx 2.612\cdots, \tag{VII.54}$$

this bound is not relevant and $n_\times = n$. However, on lowering temperature, the limiting density of excited states is achieved at

$$T_c(n) = \frac{h^2}{2\pi m k_B}\left(\frac{n}{g\zeta_{3/2}}\right)^{2/3}. \tag{VII.55}$$

For $T \leq T_c$, z gets stuck to unity ($\mu = 0$). The limiting density of excited states, $n^* = g\zeta_{3/2}/\lambda^3 \propto T^{3/2}$, is then less than the total particle density. The remaining gas particles, with density $n_0 = n - n^*$, occupy the lowest energy state with $\vec{k} = 0$. The phenomenon of a *macroscopic occupation* of a single one–particle state is known as *Bose–Einstein condensation.*

The bose condensate has some unusual properties. The gas pressure for $T < T_c$,

$$\beta P = \frac{g}{\lambda^3} f^+_{5/2}(1) = \frac{g}{\lambda^3}\zeta_{5/2} \approx 1.341\frac{g}{\lambda^3}, \tag{VII.56}$$

vanishes as $T^{5/2}$ and is *independent of density.* This is because only the excited fraction n^* has finite momentum and contributes to the pressure. Alternatively, bose condensation can be achieved at a fixed temperature by increasing density (reducing volume). From eq.(VII.54), the transition occurs at a specific volume

$$v^* = \frac{1}{n^*} = \frac{\lambda^3}{g\zeta_{3/2}}. \tag{VII.57}$$

For $v < v^*$, the pressure–volume isotherm is flat, since $\partial P/\partial v \propto \partial P/\partial n = 0$ from eq.(VII.56). The flat portion of isotherms is reminiscent of coexisting liquid and gas phases. We can similarly regard bose condensation as the coexistence of a "normal gas" of specific volume v^*, and a "liquid" of volume 0. The vanishing of the "liquid" volume is an unrealistic feature due to the absence of any interaction potential between the particles.

Bose condensation combines features of discontinuous (first order), and continuous (second order) transitions; there is a finite latent heat while the compressibility diverges. The latent heat of the transition can be obtained from the *Clausius–Clapeyron* equation which gives the change of the transition temperature with pressure as

$$\left.\frac{dT}{dP}\right|_{\text{Coexistence}} = \frac{\Delta V}{\Delta S} = \frac{T_c(v^* - v_0)}{L}. \tag{VII.58}$$

Since eq.(VII.56) gives the gas pressure right up to the transition point,

$$\left.\frac{dP}{dT}\right|_{\text{Coexistence}} = \frac{5}{2}\frac{P}{T}. \tag{VII.59}$$

Using the above equations we find a latent heat,

$$\begin{aligned} L = T_c v^* \left.\frac{dP}{dT}\right|_{\text{Coexistence}} &= \frac{5}{2} P v^* = \frac{5}{2}\frac{g}{\lambda^3}\zeta_{5/2} k_B T_c \left(\frac{g}{\lambda^3}\zeta_{3/2}\right)^{-1}, \\ \implies \qquad L &= \frac{5}{2}\frac{\zeta_{5/2}}{\zeta_{3/2}} k_B T_c \approx 1.28 k_B T_c. \end{aligned} \tag{VII.60}$$

To find the compressibility $\kappa_T = \partial n/\partial P|_T /n$, take derivatives of eqs.(VII.35), and take advantage of the identity in eq.(VII.52) to get

$$\begin{cases} \dfrac{dP}{dz} = \dfrac{g k_B T}{\lambda^3}\dfrac{1}{z} f^+_{3/2}(z) \\ \dfrac{dn}{dz} = \dfrac{g}{\lambda^3}\dfrac{1}{z} f^+_{1/2}(z) \end{cases}. \tag{VII.61}$$

The ratio of these equations leads to

$$\kappa_T = \frac{f^+_{1/2}(z)}{n k_B T f^+_{3/2}(z)}, \tag{VII.62}$$

which diverges at the transition since $\lim_{z\to 1} f^+_{1/2}(z) \to \infty$, i.e. the isotherms approach the flat coexistence portion tangentially.

From the expression for energy in the grand canonical ensemble,

$$E = \frac{3}{2}PV = \frac{3}{2} V \frac{g}{\lambda^3} k_B T f^+_{5/2}(z) \propto T^{5/2} f^+_{5/2}(z), \tag{VII.63}$$

and using eq.(VII.52), the heat capacity is obtained as

$$C_{V,N} = \left.\frac{dE}{dT}\right|_{V,N} = \frac{3}{2} V \frac{g}{\lambda^3} k_B T \left[\frac{5}{2T} f^+_{5/2}(z) + \frac{1}{z} f^+_{3/2}(z) \left.\frac{dz}{dT}\right|_{V,N}\right]. \tag{VII.64}$$

The derivative $dz/dT|_{V,N}$ is found from the condition of fixed particle number, using

$$\left.\frac{dN}{dT}\right|_{V} = 0 = \frac{g}{\lambda^3} V \left[\frac{3}{2T} f^+_{3/2}(z) + \frac{1}{z} f^+_{1/2}(z) \left.\frac{dz}{dT}\right|_{V,N}\right]. \tag{VII.65}$$

Substituting the solution

$$\frac{T}{z}\left.\frac{dz}{dT}\right|_{V,N} = -\frac{3}{2}\frac{f^+_{3/2}(z)}{f^+_{1/2}(z)},$$

into eq.(VII.64) yields

$$\frac{C_V}{Vk_B} = \frac{3}{2}\frac{g}{\lambda^3}\left[\frac{5}{2}f^+_{5/2}(z) - \frac{3}{2}\frac{f^+_{3/2}(z)^2}{f^+_{1/2}(z)}\right]. \tag{VII.66}$$

Expanding the result in powers of z indicates that at high temperatures the heat capacity is larger than the classical value; $C_V/Nk_B = 3/2[1+n\lambda^3/2^{7/2}+\cdots]$. At low temperatures, $z = 1$ and

$$\frac{C_V}{Nk_B} = \frac{15}{4}\frac{g}{n\lambda^3}\zeta_{5/2} = \frac{15}{4}\frac{\zeta_{5/2}}{\zeta_{3/2}}\left(\frac{T}{T_c}\right)^{3/2}. \tag{VII.67}$$

The origin of the $T^{3/2}$ behavior at low temperatures is easily understood. At $T = 0$ all particles occupy the $\vec{k} = 0$ state. At small but finite temperatures there is occupation of states of finite momentum, up to a value of approximately k_m such that $\hbar^2 k_m^2/2m = k_B T$. Each of these states has an energy proportional to $k_B T$. The excitation energy in d dimensions is thus given by $E_\times \propto V k_m^d k_B T$. The resulting heat capacity is $C_V \propto V k_B T^{d/2}$. The reasoning is similar to that used to calculate the heat capacities of a phonon (or photon) gas. The difference in the power laws simply originates from the difference in the energy spectrum of low energy excitations ($\mathcal{E}(k) \propto k^2$ in the former and $\mathcal{E}(k) \propto k$ for the latter). In both cases the total number of excitations is not conserved, corresponding to $\mu = 0$. For the bose gas, this lack of conservation only persists up to the transition temperature, at which point all particles are excited out of the reservoir with $\mu = 0$ at $\vec{k} = 0$. C_V is continuous at T_c, reaching a maximum value of approximately $1.92k_B$ per particle, but has a discontinuous derivative at this point.

VII.G Superfluid He^4

Interesting examples of quantum fluids are provided by the isotopes of helium. The two electrons of He occupy the 1s orbital with opposite spins. The filled orbital makes this noble gas particularly inert. There is still a van der Waals attraction between two He atoms, but the interatomic potential has a shallow minimum of depth $9^\circ K$ at a separation of roughly 3Å. The weakness of this interaction makes He a powerful *wetting agent*. As the He atoms have a stronger attraction for practically all other molecules, they easily spread over the surface of any substance. Due to its light mass, the He atom undergoes large zero point fluctuations at $T = 0$. These fluctuations are sufficient to *melt* a solid phase, and thus He remains in a liquid state at ordinary pressures. Pressures of over 25 atmosphere are required to sufficiently localize the He atoms to result in a solid phase at $T = 0$. A remarkable property of the quantum liquid at zero temperature is that, unlike its classical counterpart, it has zero entropy.

The lighter isotope of He^3 has three nucleons and obeys fermi statistics. The liquid phase is very well described by a fermi gas of the type discussed in sec.VII.E. The interactions between atoms do not significantly change the non-interacting picture described earlier. By contrast, the heavier isotope of He^4 is a boson. Helium can be cooled down by a process of evaporation: Liquid helium is placed in an isolated container, in equilibrium with the gas phase at a finite vapor density. As the helium gas is pumped out, part of the liquid evaporates to take its place. The evaporation process is accompanied by the release of latent heat which cools the liquid. The boiling liquid is quite active and turbulent, just as a boiling pot of water. However, when the liquid is cooled down to below $2.2^\circ K$, it suddenly becomes quiescent and the turbulence disappears. The liquids on the two sides of this phase transition are usually referred to as HeI and HeII.

HeII has unusual hydrodynamic properties. It flows through the finest capillaries without any resistance. Consider an experiment that pushes HeII from one container to another through a small tube packed with powder. For ordinary fluids a finite pressure difference between the containers, proportional to viscosity, is necessary to maintain the flow. HeII flows even in the limit of zero pressure difference and acts as if it has zero viscosity. For this reason it is referred to as a *superfluid*. The superflow is accompanied by heating of the container that loses HeII and cooling of the container that accepts it; the *mechano–caloric effect*. Conversely, HeII acts to remove temperature differences by flowing away from hot regions. This is the basis of the *fountain effect* in which the superfluid spontaneously moves up a tube from a heated container.

In some other circumstances HeII behaves as a viscous fluid. A classical method for measuring the viscosity of a liquid is via torsional oscillators: A collection of closely spaced disks connected to a shaft is immersed in the fluid and made to oscillate. The period of oscillations is proportional to the moment of inertia, which is modified by the quantity of fluid that is dragged by the oscillator. This experiment was performed on HeII by Andronikashvilli who indeed found a finite viscous drag. Furthermore, the changes in the frequency of the oscillator with temperature indicate that the quantity of fluid that is dragged by the oscillator starts to decrease below the transition temperature. The measured *normal density* vanishes as $T \to 0$, approximately as T^4.

In 1938, Fritz London suggested that a good starting hypothesis is that the transition to the superfluid state is related to the Bose–Einstein condensation. This hypothesis can account for a number of observations:

(1) The critical temperature of an ideal bose gas of volume $v = 46.2\text{Å}$ per particle is obtained from eq.(VII.55) as

$$T_c = \frac{h^2}{2\pi m_{\rm He} k_B} \left(v\,\zeta_{3/2}\right)^{-2/3} \approx 3.14^\circ K. \tag{VII.68}$$

The actual transition temperature of $T_c \approx 2.18^\circ K$ is not far from this value.

(2) The origin of the transition has to be related to quantum statistics as He^3, which is atomically similar, but a fermion, does not have a similar transition. (Actually He^3 does become superfluid but at temperatures of only a few $\text{m}^\circ K$. This follows a pairing of He^3 atoms which changes their statistics.)

(3) A bose condensate can account for the observed thermo–mechanical properties of HeII. The expression for pressure in eq.(VII.56) is only a function of temperature, and not density. As such, variations in pressure are accompanied by changes in temperature. This is also the reason for the absence of boiling activity in HeII. Bubbles nucleate and grow in a boiling liquid at local hot spots. In an ordinary fluid, variations in temperature relax to equilibrium only through the slow process of heat *diffusion*. By contrast if the local pressure is a function of temperature only, there will be increased pressure at a hot spot. The fluid flows in response to pressure gradients and removes them very rapidly (at the speed of sound in the medium).

(4) Hydrodynamic behavior of HeII can be explained by Tisza's *two–fluid model*, which postulates the coexistence of two components for $T < T_C$:

(a) A *normal* component of density ρ_n, moving with velocity $\vec{v}_n$, and having a finite entropy density s_n.

(b) A *superfluid* component of density ρ_s, which flows without viscosity and with no vorticity ($\nabla \times \vec{u}_s = 0$), and has zero entropy density, $s_s = 0$.

In the *super-leak* experiments, it is the superfluid component that passes through, reducing the entropy and hence temperature. In the Andronikashilli experiment, the normal component sticks to the torsional oscillator and gets dragged by it. This experiment thus gives the ratio of ρ_n to ρ_s.

There are, however, many important differences between superfluid helium and the ideal bose condensate:

(1) Interactions certainly play an important role in the liquid state. The Bose–Einstein condensate has infinite compressibility, while HeII has a finite density, related to atomic volume, and is essentially incompressible.

(2) It can be shown that, even at $T = 0$, the ideal bose condensate is not superfluid. This is because the low energy spectrum, $\mathcal{E}(\vec{k}) = \hbar^2 k^2/2m$, admits too many excitations. Any external body moving through such a fluid can easily lose energy to it by exciting these modes, leading to a finite viscosity.

(3) The detailed functional forms of the heat capacity and superfluid density are very different from their counterparts in the ideal bose condensate. The measured heat capacity diverges at the transition with a characteristic shape similar to a λ, and vanishes at low temperatures as T^3 (compared to $T^{3/2}$ for the ideal bose gas). The superfluid density obtained in the Andronikashvilli experiment vanishes as $(T_c - T)^{2/3}$ at the transition, while the normal component vanishes as approximately T^4 as $T \to 0$ (compared to $T^{3/2}$ for the condensate density in eq.(VII.53)). Understanding the nature of the singular behavior close to T_c is beyond the scope of this discussion. The behavior close to zero temperature, however, suggests a different spectrum of low energy excitations.

Based on the shape of the experimentally measured heat capacity, Landau suggested that the spectrum of low energy excitations is actually similar to that of phonons. This is a consequence of the interactions between the particles. The low energy excitations of a classical liquid are longitudinal sound waves. (In comparison, a solid admits three such excitations, two transverse and one longitudinal.) The correspondence principle suggests that quantized versions of such modes should also be present in a quantum liquid. As in the case of phonons, a linear spectrum of excitations leads to a heat capacity that vanishes as T^3. The speed of sound waves can be computed from the coefficient of the T^3 dependence as $v \approx 240 ms^{-1}$. A further anomaly in heat capacity can be explained by assuming that the spectrum of excitations bends down and has a minimum in the vicinity

of a wavenumber $k_0 \approx 2\mathring{A}^{-1}$. The excitations in the vicinity of this minimum are referred to as *rotons*, and have an energy

$$\mathcal{E}_{\text{roton}}(\vec{k}) = \Delta + \frac{\hbar^2}{2\mu}(k - k_0)^2, \tag{VII.69}$$

with $\Delta \approx 8.6^\circ K$, and $\mu \approx 0.16 m_{\text{He}}$. The spectrum postulated by Landau was confirmed directly by neutron scattering measurements in the 1950's.